Contribution from the Department of Chemistry,
Vanderbilt University, Nashville, Tennessee 37235

Synthesis and Properties of Bis(dimethyl phosphato)phenylarsine and Related Compounds

KUZHIKALAIL M. ABRAHAM and JOHN R. VAN WAZER*

Received June 5, 1975 AIC50400P

The new compounds $CH_3As[P(O)(OCH_3)_2]_2$ and $C_6H_5As[P(O)(OCH_3)_2]_2$ have been prepared and characterized from the condensation of CH_3AsI_2 and $C_6H_5AsCl_2$, respectively, with $P(OCH_3)_3$. Spectroscopic properties are in agreement with the presence of As–P bonds in these compounds. Treatment of $C_6H_5AsI_2$ with $P(OCH_3)_3$ in a 1:1 molar ratio results in the formation of $C_6H_5As(I){-}As(I)C_6H_5$. The latter iodide is also obtained by the reaction of either CH_3AsI_2 or $C_6H_5AsI_2$ with $C_6H_5As[P(O)(OCH_3)_2]_2$. When $C_6H_5AsI_2$ and $P(OCH_3)_3$ are treated in a molar ratio of 1:2, the new diarsine $[C_6H_5AsP(O)(OCH_3)_2]_2$ is obtained as a white crystalline solid. Redistribution reactions leading to the formation of $R_2P{-}P(O)(OCH_3)_2$ are observed when either $C_6H_5As[P(O)(OCH_3)_2]_2$ or $CH_3As[P(O)(OCH_3)_2]_2$ is treated with R_2PCl where R = C_6H_5 or c-C_6H_{11}.

Introduction

Much of the modern day interest in organoarsenic compounds has been in relation to transition metal chemistry, primarily for the preparation of coordination compounds. One of the areas which received comparatively less attention has been the chemistry of phosphorus derivatives of arsenic. Among these derivatives of arsenic only those containing trivalent phosphorus have been well studied.

It has been shown[1–4] by means of NMR spectroscopy that condensation reactions involving chloro- and methoxyphosphines (i.e., R_xPCl_{3-x}, where $x = 1$ or 2, with $R_yP(OCH_3)_{3-y}$, where $y = 0$, 1, or 2, and R = akyl or aryl group) resulted in products which possess P–P bonds, according to eq 1.

$$R_xPCl_{3-x} + R_yP(OCH)_{3-y} \rightarrow Cl_{2-x}(R_x)P{-}P(O)(R_y)(OCH_3)_{2-y} + CH_3Cl \quad (1)$$

Although a few compounds containing both phosphorus and arsenic in the same molecule have been prepared[5] by an analogous reaction between dimethylhaloarsines and trialkyl phosphites, it has not been established definitely whether these compounds possess a "phosphate" $[R_2As{-}P(O)(OCH_3)_2]$ or a "phosphite" $[R_2As{-}O{-}P(OCH_3)_2]$ structure. A good way to distinguish between these two structures is by means of ^{31}P NMR spectroscopy, since it is known[6] that fully esterified phosphites (triply connected phosphorus) exhibit ^{31}P chemical shifts which are considerably more negative than those of the analogous phosphates. In the known $R_2P{-}P(O)(OCH_3)_2$ compounds,[1,3,4] which possess direct P–P bonds as evidenced by the characteristic PP coupling constants, the ^{31}P resonance of the $-P(O)(OCH_3)_2$ moiety is found between −43 and −35 ppm. It should be noted that these values are very much in the range—between 0 and −50 ppm—found for phosphates, phosphonates, and phosphinates. On the other hand, most of the known phosphites, phosphinites, or phosphonites exhibit chemical shifts which are around or below −100 ppm.

The presence of an As–P bond in $R_2As{-}P(O)(OCH_3)_2$ should also be evident from the characteristic P═O stretching vibration between 1150 and 1250 cm^{-1} in the infrared (ir) spectra of these compounds. The spectroscopic as well as chemical properties of the various compounds described in this paper indicate that, indeed, the condensation product from a chloroarsine and a trialkyl phosphite has an As–P bond.

Experimental Section

Unless otherwise stated, all reactions in this study were carried out in the absence of air and moisture. A drybag or a drybox was employed wherever appropriate. Preparations were carried out either in sealed-glass tubes or in three-necked flasks under an atmosphere of nitrogen and the filtration and transfer of the products were done strictly under nitrogen.

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 with signal accumulation while the proton spectra were taken in the continuous wave mode. It was possible to employ broad-band proton decoupling 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. The ^1H chemical shifts were measured with respect to CH_2Cl_2, with the chemical shift of this compound being taken as +5.35 ppm with respect to $(CH_3)_4Si$ and positive shifts being downfield from the $(CH_3)_4Si$ reference.

Infrared spectra were obtained on a Perkin-Elmer Model 727 spectrometer using KBr cells.

Dichlorophenylarsine and diiodomethylarsine were purchased from Ventron Corp., Beverly, Mass. Diiodophenylarsine came from Eastman Organic Chemicals, Rochester, N.Y. These reagents were used as obtained. Trimethyl phosphite was procured from Aldrich Chemical Co., Inc., Milwaukee, Wis., and chlorodiphenyl- and chlorodicyclohexylphosphine were purchased from Strem Chemicals, Inc., Danvers, Mass. All of the phosphorus reagents exhibited the proper boiling points and were found to be pure according to their ^{31}P NMR spectra. The CH_2Cl_2, which was of Spectrograde quality, was dried over phosphorus pentoxide and then distilled.

Synthesis of $C_6H_5As[P(O)(OCH_3)_2]_2$. In a standard preparation, 4 g (17.9 mmol) of $C_6H_5AsCl_2$ was mixed with a solution of 4.9 g (39.5 mmol) of $P(OCH_3)_3$ in 1.5 ml of CH_2Cl_2 in a sealed, evacuated glass tube. It was kept at room temperature for about 20 h while the tube was shaken occasionally. Thereafter, the volatile materials were removed under vacuum to obtain $C_6H_5As[P(O)(OCH_3)_2]_2$ as a colorless liquid; yield 6.3 g (95% based on the $C_6H_5AsCl_2$ used). Anal. Calcd for $C_{10}H_{17}AsP_2O_6$: C, 32.43; H, 4.59; As, 20.24; P, 16.75; O, 25.94. Found: C, 32.20; H, 4.50; As, 19.80; P, 16.20. NMR: proton, $\delta_{C_6H_5}$ 7.85, 7.35 ppm (multiplets 2:3, 5 H), δ_{OCH_3} 3.59 ppm (pair of doublets, 12 H), J_{POCH} = 12 Hz; phosphorus (^1H decoupled), −30.9 ppm (singlet). Ir: 3050 (m), 3000 (m), 2950 (s), 2850 (m), 1480 (m), 1460 (m), 1435 (m), 1240 (s), 1180 (m), 1020 (vs, br), 810 (s), 740 (s), 690 (m) cm^{-1}.

Synthesis of $CH_3As[P(O)(OCH_3)_2]_2$. In a representative synthesis, 2.3 g (6.6 mmol) of CH_3AsI_2 was mixed with a solution of 1.9 g (15.3 mmol) of $P(OCH_3)_3$ in 1 ml of CH_2Cl_2 in a sealed, evacuated glass tube. The mixture was kept at room temperature for 3 h with intermittent shaking. After work-up, as described above, $CH_3As[P(O)(OCH_3)_2]_2$ was obtained as a colorless liquid; yield 1.9 g (93% based on the CH_3AsI_2 used). Anal. Calcd for $C_5H_{15}AsP_2O_6$: C, 19.48; H, 4.87; As, 24.35; P, 20.12; O, 31.16. Found: C, 19.0; H, 4.6; As, 24.0; P, 19.5. NMR: proton, δ_{CH_3} 1.35 ppm (triplet, 3 H), J_{PAsCH} = 16.5 Hz, δ_{OCH_3} 3.65 ppm (pair of doublets, 12 H), J_{POCH} = 10 Hz; phosphorus (^1H decoupled), −33.5 ppm (singlet). Ir: 3000 (m), 2950 (s), 2850 (m), 1460 (m), 1405 (w), 1230 (s), 1175 (m), 1020 (vs, br), 850 (w), 800 (s), 740 (s) cm^{-1}.

Syntheses of $C_6H_5As(I){-}As(I)C_6H_5$. 1. From $C_6H_5AsI_2$ and $P(OCH_3)_3$. In this synthesis, 2.6 g (6.4 mmol) of $C_6H_5AsI_2$ was combined with a solution of 0.83 g (6.7 mmol) of $P(OCH_3)_3$ in 1.5 ml of CH_2Cl_2 in a sealed, evacuated glass tube. On warming of the mixture to ambient temperature, an exothermic reaction ensued with concomitant precipitation of the product as a deep yellow solid. After about 1 h, this solid was filtered, washed several times with methylene chloride, and dried under vacuum; mp 175–177 °C (lit.[8] mp 176–177 °C); yield 0.74 g (41% based on the $C_6H_5AsI_2$ used). Anal. Calcd for $C_{12}H_{10}As_2I_2$: C, 25.8; H, 1.79; As, 26.88; I, 45.51. Found: C, 25.0; H, 1.6; As, 26.2, I, 45.1.

The filtrate was analyzed by ^{31}P NMR spectroscopy to have contained, besides CH_2Cl_2, the compounds $C_6H_5As[P(O)(OCH_3)_2]_2$ (−30.9 ppm), $C_6H_5As(I)[P(O)(OCH_3)_2]$ (−21.7 ppm), and $(CH_3O)_2P(O)I$ (−2.3 ppm).

2. From $C_6H_5AsI_2$ and $C_6H_5As[P(O)(OCH_3)_2]_2$. A mixture containing 1.9 g (5.1 mmol) of $C_6H_5As[P(O)(OCH_3)_2]_2$ and 1.8 g (4.4 mmol) of $C_6H_5AsI_2$ in 0.5 ml of CH_2Cl_2 was kept in a sealed, evacuated glass tube at ambient temperature for 10 days. The yellow product obtained was worked up as above; yield 0.53 g (22%); mp 170–173 °C.

The filtrate was found to contain, besides CH_2Cl_2 and starting materials, $C_6H_5As(I)[P(O)(OCH_3)_2]$ and $(CH_3O)_2P(O)I$ according to ^{31}P NMR spectroscopy.

3. From CH_3AsI_2 and $C_6H_5As[P(O)(OCH_3)_2]_2$. A mixture containing 1.8 g (4.9 mmol) of $C_6H_5As[P(O)OCH_3]_2$ and 1.1 g (3.2 mmol) of CH_3AsI_2 in 1 ml of CH_2Cl_2 was kept in a sealed, evacuated glass tube at ambient temperature for 3 h. The yellow product which precipitated was filtered and dried under vacuum; mp 174–176 °C; yield 0.52 g (29%).

The filtrate from the reaction mixture contained, besides CH_2Cl_2 and starting materials, $C_6H_5As(I)[P(O)(OCH_3)_2]$, $CH_3As[P(O)(OCH_3)_2]_2$, $CH_3As(I)[P(O)(OCH_3)_2]$ (−23.8 ppm), and $(CH_3O)_2P(O)I$, as evidenced by ^{31}P NMR spectroscopy.

Syntheses of $[C_6H_5AsP(O)(OCH_3)_2]_2$. 1. From $C_6H_5AsI_2$ and $P(OCH_3)_3$. In a typical synthesis, 2.7 g (6.6 mmol) of $C_6H_5AsI_2$ was mixed with 1.6 g (12.8 mmol) of $P(OCH_3)_3$ in 1 ml of CH_2Cl_2, in a sealed, evacuated glass tube. Upon mixing at room temperature, an exothermic reaction ensued, with the simultaneous precipitation of a yellow solid. This yellow solid disappeared in about 1 h with the formation of a white precipitate and a clear solution. After being kept at room temperature for 1 day, the tube was opened and all of the volatile materials were removed under vacuum. To the resulting pasty mixture 2 ml of hexane was added and the solid was removed by filtration. The white solid product was washed several times with hexane and then dried under vacuum; mp 125–131 °C; yield 1.24 g (71.5% based on the $C_6H_5AsI_2$ used). Anal. Calcd for $C_{16}H_{22}As_2P_2O_6$: C, 36.78; H, 4.21; As, 28.73; P, 11.87; O, 18.39. Found: C, 36.5; H, 4.3; As, 27.4; P, 11.5. NMR: proton (CH_2Cl_2 solution), $\delta_{C_6H_5}$ 8.05, 7.78, 7.51, 7.25 ppm (all multiplets), δ_{OCH_3} 3.75 (doublet), 3.5 (doublet), 3.20 ppm (complex multiplet of six resonances); the ratio of $\sum C_6H_5$ to $\sum OCH_3$ is 1.3; phosphorus (^1H decoupled), −35.4 ppm (two closely lying peaks having intensity ratio of ca. 3:1). Ir: 3050 (m), 3000 (m), 2950 (s), 2830 (m), 1470 (m), 1445 (m), 1425 (m), 1235 (s), 1175 (s), 1030 (vs), 800 (s), 750 (s), 695 (m) cm^{-1}.

The filtrate from the separation of $[C_6H_5AsP(O)(OCH_3)_2]_2$ contained $C_6H_5As[P(O)(OCH_3)_2]_2$, as evidenced by spectral data.

2. From $C_6H_5As(I){-}As(I)C_6H_5$ and $P(OCH_3)_3$. In a reaction, 0.61 g (1.1 mmol) of $C_6H_5As(I){-}As(I)C_6H_5$ was stirred with 0.5 g (4 mmol) of $P(OCH_3)_3$ in 2 ml of CH_2Cl_2 under nitrogen for about 1 h. During this time a white solid and a clear solution were observed. After work-up as described above, 0.36 g (34% yield) of the product was obtained. The filtrate from this reaction contained some $C_6H_5As[P(O)(OCH_3)_2]_2$.

The mass spectrum of $[C_6H_5AsP(O)(OCH_3)_2]_2$ recorded at an ionization voltage of 70 eV, with direct introduction of the sample, showed the parent peak at m/e 522. Other prominent peaks in the spectrum which served to identify the compound were m/e 413 $[C_6H_5(CH_3O)_2(O)PAs{-}AsC_6H_5^+]$, 261 $[(C_6H_5)CH_3O)_2(O)PAs^+]$, 227 $[C_6H_5As_2^+]$, 152 $[C_6H_5As^+]$, 109 $[(CH_3O)_2P(O)^+]$, and 93 $[(CH_3O)_2P^+]$.

Reactions of $RAs[P(O)(OCH_3)_2]_2$, Where R = C_6H_5 or CH_3, with $(C_6H_5)_2PCl$ or $(C_6H_{11})_2PCl$. All these reactions were carried out in 5-mm NMR tubes with weighed quantities of the reagents, using CH_2Cl_2 as solvent. The products were identified by comparison of their NMR spectral properties with those of authentic samples. (See Results and Discussion for details.)

Reaction of $CH_3As[P(O)(OCH_3)_2]_2$ with CH_3AsI_2. The reaction was carried out with weighed quantities of the reagents in 5-mm NMR tubes and the products were identified from NMR spectral data.

Reaction of $C_6H_5As[P(O)(OCH_3)_2]_2$ with $C_6H_5AsCl_2$. A mixture containing 0.41 g (1.1 mmol) of $C_6H_5As[P(O)(OCH_3)_2]_2$ and 0.63 g (2.82 mmol) of $C_6H_5AsCl_2$ in 0.5 ml of CH_2Cl_2 did not show any evidence for reaction even after 1 month at room temperature or heating at 80 °C for 20 h.

Results and Discussion

When dichlorophenylarsine, $C_6H_5AsCl_2$, is combined with trimethyl phosphite, $P(OCH_3)_3$, in methylene chloride at room temperature in a molar ratio of 1:2, bis(dimethyl phosphato)phenylarsine, $C_6H_5As[P(O)(OCH_3)_2]_2$, I, is produced in a quantitative fashion according to eq 2. The stoichiometry

$$C_6H_5AsCl_2 + 2P(OCH_3)_3 \rightarrow C_6H_5As[P(O)(OCH_3)_2]_2 + 2CH_3Cl \tag{2}$$

of the reaction is verified by quantitative NMR (^1H and ^{31}P) studies on reaction mixtures of known compositions. Qualitative kinetic studies have shown that the reaction is complete in ca. 5 h. The new compound, $C_6H_5As[P(O)(OCH_3)_2]_2$, is the first characterized representative in the family of compounds, $RAs[P(O)(OR')_2]_2$, where R, R' = alkyl or aryl groups. It is isolated as a colorless, air-sensitive liquid and is stable at room temperature under nitrogen for an indefinite period.

The structural evidence for this compound is obtained from ^{31}P NMR and ir spectra. The ^1H-decoupled ^{31}P NMR spectrum of I exhibits a singlet at −30.9 ppm. This is close to the values found for the $-P(O)(OCH_3)_2$ moiety in $(C_6H_5)_2P{-}P(O)(OCH_3)_2$[1] (−35.7 ppm), in $C_6H_5P[P(O)(OCH_3)_2]_2$[1] (−33.7 ppm), and in the various phosphate and phosphonate esters.[6] On the other hand, the isomeric phosphite moiety $-OP(OCH_3)_2$ usually exhibits ^{31}P chemical shifts below −100 ppm. Although ^{75}As (100% abundant) has a spin of $^3/_2$, it does not show coupling with the phosphorus resonance. This is probably due to the large quadrupolar interaction.[7] Further evidence for this structure is obtained from the infrared spectrum which shows a strong P=O stretching frequency at 1240 cm^{-1}. In the related compounds $(C_6H_{11})_2P{-}P(O)(OCH_3)_2$ and $(t\text{-}C_4H_9)_2P{-}P(O)(OCH_3)_2$, the P=O stretching bands are found[4] at 1230 and 1235 cm^{-1}, respectively.

In the proton NMR spectrum, the methoxyl groups of I are observed as a pair of doublets with J_{POCH} = 12 Hz. It may be noted that the methoxyl groups on each phosphorus atom are diastereomeric and therefore they are magnetically nonequivalent. The two nonequivalent methoxyl groups when coupled with the phosphorus atom give rise to a pair of doublets. The observed ratio of the intensity of the methoxyl protons to that of the phenyl protons is 2.45 as opposed to the calculated value of 2.4.

Bis(dimethyl phosphato)methylarsine, $CH_3As[P(O)(OCH_3)_2]_2$, II, is obtained from CH_3AsI_2 and $P(OCH_3)_3$, as shown in eq 3. Its NMR and ir spectral features are, again, in

$$CH_3AsI_2 + 2P(OCH_3)_3 \rightarrow CH_3As[P(O)(OCH_3)_2]_2 + 2CH_3I \tag{3}$$

agreement with a direct As–P bond. One noteworthy feature in the proton NMR spectrum is the triplet (1:2:1) of the arsenic–methyl group which results from the coupling of the two phosphorus atoms with the methyl protons. The J value of 16.5 Hz is comparable to PH coupling constants in compounds where phosphorus and hydrogen are separated by two other atoms.[6] This is further evidence for an As–P bond in II.

Unlike the reaction between $C_6H_5AsCl_2$ and $P(OCH_3)_3$, a series of products is obtained upon combining $C_6H_5AsI_2$ with $P(OCH_3)_3$, the nature of the products being dependent upon the initial molar ratio of the reagents. When $C_6H_5AsI_2$ and $P(OCH_3)_3$ are combined in CH_2Cl_2 at room temperature, an exothermic reaction occurs with the precipitation of the known iodide, $C_6H_5As(I)-As(I)C_6H_5$, III. Compound III is identified from elemental analysis and from its melting point.[8] The ^{31}P NMR spectrum of the filtrate from the reaction mixture after the removal of $C_6H_5As(I)-As(I)C_6H_5$ contained three peaks: one at −30.9 ppm due to $C_6H_5As[P(O)(OCH_3)_2]_2$ and the other two at −21.7 and −2.3 ppm. The peak at −21.7 ppm was identified as being due to $C_6H_5As(I)[P(O)(OCH_3)_2]$ by treating the filtrate with $P(OCH_3)_3$, whereupon this compound was quantitatively converted to $C_6H_5As[P(O)(OCH_3)_2]_2$. The peak at −2.3 ppm was assigned to $(CH_3O)_2P(O)I$ on the basis of its ^1H-undecoupled ^{31}P NMR spectrum (septet) as well as on the basis of this resonance being close to that for $(CH_3O)_2P(O)Cl$ (−6.4 ppm).[6] The formation of $C_6H_5As(I)-As(I)C_6H_5$ may be explained by assuming that $C_6H_5AsI_2$ first reacts with $P(OCH_3)_3$ to produce $C_6H_5As(I)[P(O)(OCH_3)_2]$. The latter iodide can then react either with $P(OCH_3)_3$ to produce $C_6H_5As[P(O)(OCH_3)_2]_2$ or with $C_6H_5AsI_2$ to form $C_6H_5As(I)-As(I)C_6H_5$, as shown in eq 4–6.

$$C_6H_5AsI_2 + P(OCH_3)_3 \rightarrow C_6H_5As(I)[P(O)(OCH_3)_2] + CH_3I \tag{4}$$

$$C_6H_5As(I)[P(O)(OCH_3)_2] + P(OCH_3)_3 \rightarrow C_6H_5As[P(O)(OCH_3)_2]_2 + CH_3I \tag{5}$$

$$C_6H_5As(I)[P(O)(OCH_3)_2] + C_6H_5AsI_2 \rightarrow C_6H_5As(I)-As(I)C_6H_5 + (CH_3O)_2P(O)I \tag{6}$$

The reaction sequence in eq 4 and 6 leading to formation of $C_6H_5As(I)-As(I)C_6H_5$ is verified by the preparation of this compound from $C_6H_5AsI_2$ and $C_6H_5As[P(O)(OCH_3)_2]_2$. A qualitative kinetic study by NMR of the interaction between these two reagents has shown that $C_6H_5As(I)P(O)(OCH_3)_2$ is formed initially (eq 7), before the precipitation of $C_6H_5As(I)-As(I)C_6H_5$.

$$C_6H_5AsI_2 + C_6H_5As[P(O)(OCH_3)_2]_2 \rightarrow 2C_6H_5As(I)[P(O)(OCH_3)_2] \tag{7}$$

It is noteworthy that the reaction shown in eq 6 is quite analogous to the one[3] (eq 8) leading to the formation of tetraphenyldiphosphine, $(C_6H_5)_2P-P(C_6H_5)_2$, when $(C_6H_5)_2P-P(O)(CH_3)OCH_3$ is treated with $(C_6H_5)_2PCl$.

$$(C_6H_5)_2P-P(O)(CH_3)OCH_3 + (C_6H_5)_2PCl \rightarrow CH_3P(O)(OCH_3)Cl + (C_6H_5)_2P-P(C_6H_5)_2 \tag{8}$$

The diarsine, III, was previously synthesized from the reaction of $C_6H_5AsI_2$ with phosphorous acid, $P(OH)_3$. It is quite conceivable that the compound $C_6H_5As(I)P(O)(OH)_2$ may have been an intermediate in that reaction.

The iodide $C_6H_5As(I)-As(I)C_6H_5$ can also be prepared by treating $C_6H_5As[P(O)(OCH_3)_2]_2$ with CH_3AsI_2. Here, $C_6H_5As(I)[P(O)(OCH_3)_2]$ and $C_6H_5AsI_2$ are initially produced by the redistribution reactions depicted in eq 9–11. The iodide $C_6H_5As(I)-As(I)C_6H_5$ was separated and characterized.

$$CH_3AsI_2 + C_6H_5As[P(O)(OCH_3)_2]_2 \rightarrow C_6H_5As(I)[P(O)(OCH_3)_2] + CH_3As(I)[P(O)(OCH_3)_2] \tag{9}$$

$$CH_3AsI_2 + C_6H_5As(I)[P(O)(OCH_3)_2] \rightarrow C_6H_5AsI_2 + CH_3As(I)[P(O)(OCH_3)_2] \tag{10}$$

$$CH_3As(I)[P(O)(OCH_3)_2] + C_6H_5As[P(O)(OCH_3)_2]_2 \rightarrow C_6H_5As(I)[P(O)(OCH_3)_2] + CH_3As[P(O)(OCH_3)_2]_2 \tag{11}$$

The other products $CH_3As[P(O)(OCH_3)_2]_2$, $CH_3As(I)[P(O)(OCH_3)_2]$ and $C_6H_5As(I)[P(O)(OCH_3)_2]$ were characterized from the ^{31}P NMR spectra of the filtrate after separating $C_6H_5As(I)-As(I)C_6H_5$. As before, addition of $P(OCH_3)_3$ caused the disappearance of the peaks assigned to the mixed monomers so that only the resonances of I and II were observed in the resulting solution.

It should be noted that there was no reaction between $C_6H_5As[P(O)(OCH_3)_2]_2$ and $C_6H_5AsCl_2$, even after 1 month at room temperature. This observation agrees with the previously reported[8] failure to prepare $C_6H_5As(Cl)-As(Cl)C_6H_5$ from $C_6H_5AsCl_2$ and phosphorous acid.

When CH_3AsI_2 (1.4 mmol) is combined with $CH_3As[P(O)(OCH_3)_2]_2$ (1.2 mmol) in CH_2Cl_2 at room temperature, they react with the complete disappearance of the latter compound, II, in about 100 h. In the proton NMR spectrum, the 1:2:1 triplet corresponding to the CH_3As group of II is replaced by the singlets at 1.91 and 1.85 ppm with a peak intensity ratio of ~4:1. These two peaks are close to the previously reported[9] CH_3As resonance for the $[CH_3As]_n$ polymer. In addition, some CH_3I is also formed which, however, is observed only after much of the $CH_3As[P(O)(OCH_3)_2]_2$ has reacted with CH_3AsI_2. In the ^{31}P NMR spectrum at the initial stage of the reaction, the resonance corresponding to $(CH_3O)_2P(O)(I)$ (−2.3 ppm) is observed. This is followed by the appearance of a series of peaks at +10 ppm and another series of peaks at +25 ppm. These two series are in the region found for $(CH_3O)_2P(O)O-$ end groups and $-O-(CH_3O)P(O)-O-$ middle groups, respectively. The disappearance of the CH_3As triplet even at the initial stages of the reaction tends to indicate that the As–P bond in $CH_3As[P(O)(OCH_3)_2]_2$ is cleaved by CH_3AsI_2 to form $(CH_3O)_2P(O)I$. This reaction is similar to the one observed in the system of $C_6H_5AsI_2$ and $C_6H_5As[P(O)(OCH_3)_2]_2$. However, the arsenic moiety ($CH_3As<$) seems to be incorporated in polymeric structures,[10] $[CH_3As]_n$. As the reaction proceeds, $(CH_3O)_2P(O)I$ probably undergoes self-condensation to produce CH_3I and polyphosphates. These ideas may be summarized by eq 12–14. Note that the interaction between CH_3AsI_2 and $CH_3As[P(O)(OCH_3)_2]_2$ is analogous to the one[9] between CH_3AsH_2 and CH_3AsI_2 producing $[CH_3As]_n$.

$$CH_3As[P(O)(OCH_3)_2]_2 + CH_3AsI_2 \rightarrow CH_3As(I)-As(CH_3)[P(O)(OCH_3)_2] + (CH_3O)_2P(O)I \tag{12}$$

$$(n/2)CH_3As(I)-As(CH_3)[P(O)(OCH_3)_2] \rightarrow [CH_3As]_n + (n/2)(CH_3O)_2P(O)I \tag{13}$$

$$(CH_3O)_2P(O)I \rightarrow CH_3I + \text{condensed phosphates} \tag{14}$$

The difference in reactivity between the systems of $C_6H_5AsI_2-C_6H_5As[P(O)(OCH_3)_2]_2$ and $CH_3AsI_2-CH_3As[P(O)(OCH_3)_2]_2$ may be attributed to kinetic factors. Our observation compares well with the previously reported reactivities of arsenobenzene, $(C_6H_5As)_n$, and arsenomethane, $(CH_3As)_n$, with I_2. With arsenobenzene and iodine the product was $C_6H_5As(I)-As(I)C_6H_5$,[8] whereas high molecular weight polymers[11] containing As–As bonds were obtained from arsenomethane and iodine.

1,2-Diphenyl-1,2-bis(dimethyl phosphato)diarsine, $[C_6H_5AsP(O)(OCH_3)_2]_2$. The new compound $[(CH_3O)_2(O)P](C_6H_5)As-As(C_6H_5)[P(O)(OCH_3)_2]$, IV, represents the first characterized example of any molecule containing an As–P bond in which two phosphorus atoms are bridged by the diarsine unit, >As–As<. It is obtained as a white air-sensitive crystalline solid. Its structure is established from elemental analysis as well as from its preparation from $C_6H_5As(I)-As(I)C_6H_5$ and $P(OCH_3)_3$, eq 15. The mass spectrum of the compound shows the parent peak at *m/e* 522.

$$C_6H_5As(I)-As(I)C_6H_5 + 2P(OCH_3)_3 \rightarrow [C_6H_5AsP(O)(OCH_3)_2]_2 + 2CH_3I \tag{15}$$

Other prominent ion fragments in the mass spectrum are also in agreement with the proposed structure. This diarsine derivative may be prepared directly from $C_6H_5AsI_2$ and $P(OCH_3)_3$ by treating them in methylene chloride at room temperature in a molar ratio of 1:2 whereby it is formed along with $C_6H_5As[P(O)(OCH_3)_2]_2$. Its ^{31}P and ^1H NMR spectra may be interpreted to support the assigned structure.

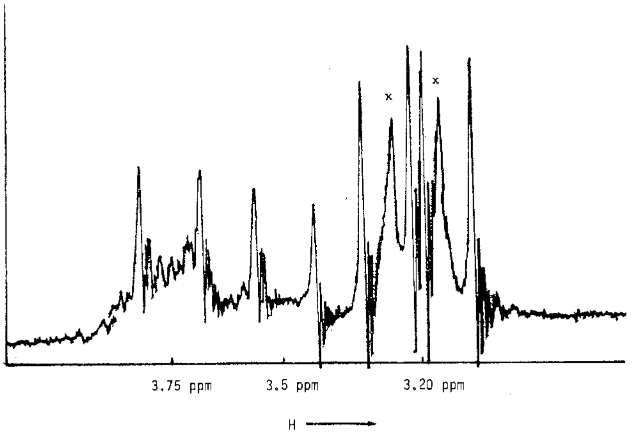

Figure 1. The 100-MHz ^1H spectrum of $[C_6H_5AsP(O)(OCH_3)_2]_2$ in the methoxyl region recorded in the continuous wave mode at a spectral sweep width of 270 Hz.

Before proceeding to a discussion of the NMR spectra, it is necessary to consider some steriochemical aspects of trivalent arsenic.[12,13] It has been established that because of its configurational stability, trivalent arsenic is capable of supporting optical activity. Thus the proton NMR spectrum of $C_6H_5(CH_3)As–As(CH_3)C_6H_5$ shows two methyl resonances which are assigned to the meso and *dl* forms.[14] By analogy, $[(CH_3O)_2(O)P](C_6H_5)As–As(C_6H_5)[P(O)(OCH_3)_2]$, IV, may also be expected to exist in the meso and *dl* forms. The reproducible ^1H-decoupled ^{31}P spectrum of IV shows two peaks (ca. 3:1 area ratio) separated by ~3 Hz which are assigned to the meso and *dl* forms but are not distinguishable. The proton NMR spectrum in the phenyl region exhibits four multiplets centered at 8.05, 7.51, 7.78 and 7.25 ppm. The ratio of the intensity of the peak at 8.05 ppm to that at 7.51 ppm and of the peak at 7.78 ppm to that at 7.25 ppm is 2:3. The area ratio of the first pair of these multiplets to the second pair is again ca. 3:1. It may be noted here that in the proton NMR spectrum of $C_6H_5As[P(O)(OCH_3)_2]_2$, the phenyl resonances were found as two multiplets centered at 7.85 ppm (ortho H) and 7.35 ppm (para and meta H) with an intensity ratio of 2:3. The observed four multiplets in the spectrum of $[C_6H_5AsP(O)(OCH_3)_2]_2$ suggest that they may be due to the phenyl groups of the two diastereomers.

The methoxyl region of the proton spectrum of IV exhibits a somewhat complex resonance pattern (Figure 1) in which the upfield group of resonances exhibits a 3:1 area ratio with respect to the downfield group. Even if the various rotational barriers are low, the presence of optical activity at the arsenic atoms leads to nonequivalence of the methoxyl groups on a given phosphorus atom. This situation would lead to eight resonance peaks in Figure 1. The additional two peaks (marked X in the figure) may result from restricted rotation; and, since they are broader than the other resonances, each may be a closely lying doublet.

$$2(C_6H_5)_2PCl + C_6H_5As[P(O)(OCH_3)_2]_2 \rightarrow 2(C_6H_5)_2P\text{-}P(O)(OCH_3)_2 + C_6H_5AsCl_2 \qquad (16)$$

$$2(C_6H_5)_2PCl + CH_3As[P(O)(OCH_3)_2]_2 \rightarrow 2(C_6H_5)_2P\text{-}P(O)(OCH_3)_2 + CH_3AsCl_2 \qquad (17)$$

Reactions of $RAs[P(O)(OCH_3)_2]_2$ with R'_2PCl, Where R = CH_3 or C_6H_5 and R' = C_6H_5 or C_6H_{11}. When $C_6H_5As[P(O)(OCH_3)_2]_2$ or $CH_3As[P(O)(OCH_3)_2]_2$ is treated with $(C_6H_5)_2PCl$ in methylene chloride, redistribution reactions 16 and 17 take place in a quantitative fashion. The diphosphine monoxide $(C_6H_5)_2P–P(O)(OCH_3)_2$ was identified from its ^{31}P NMR spectrum[2] which was identical with the one observed for a sample prepared from $(C_6H_5)_2PCl$ and $P(OCH_3)_3$—δ_{P_A} +34.26 ppm; δ_{P_B} −35 ppm; $J_{P_AP_B}$ = 191 Hz. Although the reaction shown in eq 16 took ca. 15 hr for completion, the one in eq 17 was complete in about 2 h. A similar reaction was also observed between $(C_6H_{11})_2PCl$ and $RAs[P(O)(OCH_3)_2]_2$ to form[4] $(C_6H_{11})_2P–P(O)(OCH_3)_2$—$\delta_{P_A}$ +21.5 ppm; δ_{P_B} −42.6 ppm; $J_{P_AP_B}$ = 253 Hz. However, the reaction with $(C_6H_{11})_2PCl$ was about 10 times slower than that with $(C_6H_5)_2PCl$. In the reactions described above, after the initial exchange processes, further reactions were noticed. However, these were not explored. The observed preference by the $-P(O)(OCH_3)_2$ moiety for R_2P- over $RAs<$ in these reactions may be partially attributed to the better pπ–dπ electron overlap achieved in the formation of the bond between two equally sized phosphorus atoms than between a phosphorus and an arsenic atom of unequal sizes. Another contributing factor may be the greater electropositivity associated with arsenic than with phosphorus, a situation which leads to an affinity of chlorine toward arsenic. It is interesting to note that in the scrambling[15] of oxygen vs. chlorine between the $:As\equiv$ and $OP\equiv$ moieties, the chlorine preferentially transfers to the arsenic atoms. In many respects, this exchange is similar to the scrambling of phosphorus vs. chlorine between these two moieties, as shown in eq 16 and 17.

Acknowledgment. We wish to thank the National Science Foundation for partial support of this work under Research Grant GP-28698X.

Registry No. $C_6H_5As[P(O)(OCH_3)_2]_2$, 58167-59-2; $CH_3As[P(O)(OCH_3)_2]_2$, 58167-60-5; $C_6H_5As(I)–As(I)C_6H_5$, 58167-61-6; $[C_6H_5AsP(O)(OCH_3)_2]_2$, 58167-62-7; $C_6H_5As(I)[P(O)(OCH_3)_2]$, 58167-63-8; $CH_3As(I)[P(O)(OCH_3)_2]$, 58167-64-9; $(CH_3O)_2P(O)I$, 29197-76-0; $(C_6H_5)_2P–P(O)(OCH_3)_2$, 17052-22-1; $(C_6H_{11})_2P–P(O)(OCH_3)_2$, 58167-65-0; $P(OCH_3)_3$, 121-45-9; $C_6H_5AsCl_2$, 696-28-6; CH_3AsI_2, 7207-97-8; $C_6H_5AsI_2$, 6380-34-3; $(C_6H_5)_2PCl$, 1079-66-9; $(C_6H_{11})_2PCl$, 16523-54-9.

References and Notes

(1) E. Fluck and H. Binder, *Inorg. Nucl. Chem. Lett.*, **3**, 307 (1967).
(2) K. M. Abraham and J. R. Van Wazer, *Inorg. Chem.*, **13**, 2346 (1974).
(3) K. M. Abraham and J. R. Van Wazer, *Inorg. Chem.*, **14**, 1099 (1975).
(4) K. M. Abraham and J. R. Van Wazer, *Phosphorus*, **6**, 23 (1975).
(5) G. M. Kosolapoff and L. Maier, *Org. Phosphorus Compd.*, **1**, 402 (1972).
(6) V. Mark, C. H. Dungan, M. Crutchfield, and J. R. Van Wazer, *Top. Phosphorus Chem.*, **5**, 236 (1967).
(7) R. K. Harris and R. G. Hayter, *Can. J. Chem.*, **42**, 2282 (1964).
(8) F. F. Blicke and F. D. Smith, *J. Am. Chem. Soc.*, **52**, 2937 (1930).
(9) A. L. Rheingold, J. E. Lewis, and J. M. Bellama, *Inorg. Chem.*, **12**, 2845 (1973).
(10) F. Knoll, H. C. Marsmann, and J. R. Van Wazer, *J. Am. Chem. Soc.*, **91**, 4986 (1969).
(11) M. Ya. Kraft and V. V. Katyshkina, *Dokl. Akad. Nauk SSSR*, **65**, 509 (1949); *Chem. Abstr.*, **45**, 2890 (1951).
(12) V. I. Sokolov and O. A. Rentov, *Russ. Chem. Rev. (Engl. Transl.)*, **34**, 1 (1965).
(13) K. Mislow, "Introduction to Stereochemistry", W. A. Benjamin, New York, N.Y., 1966, p 87.
(14) J. B. Lambert, G. F. Jackson, III, and D. C. Mueller, *J. Am. Chem. Soc.*, **90**, 6401 (1968).
(15) J. R. Van Wazer and K. Moedritzer, *J. Am. Chem. Soc.*, **90**, 47 (1968). [See Figure 3 and related text.]