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THE REDUCTION OF DICHLOROPHENYL- AND CHLORODIPHENYL-ARSINES WITH DIMETHOXYMETHYLPHOSPHINE TO FORM AN As—As BOND

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Summary

Treatment of 1 mol of $C_6H_5AsCl_2$ with 2 mol or an excess of $CH_3P(OCH_3)_2$ at room temperature produces $C_6H_5As[P(O)(CH_3)(OCH_3)]_2$. NMR spectroscopic evidence suggests that this compound exists in three diastereoisomeric forms. when an excess of $C_6H_5AsCl_2$ is treated with $CH_3P(OCH_3)_2$ or when $C_6H_5As[P(O)(CH_3)(OCH_3)]_2$ is treated with $C_6H_5AsCl_2$, $(C_6H_5As)_6$ is produced. Similarly $(C_6H_5)_2As—As(C_6H_5)_2$ is obtained from either 2 mol of $(C_6H_5)_2AsCl$ and 1 mol of $CH_3P(OCH_3)_2$ or by the reaction of $(C_6H_5)_2AsCl$ with $(C_6H_5)_2AsP(O)(CH_3)OCH_3$. Under the experimental conditions employed in this study $P(OCH_3)_3$ failed to reduce either $C_6H_5AsCl_2$ or $(C_6H_5)_2AsCl$ to yield As—As bonded compounds.

Introduction

In a study reported [1] recently by us it was found that the final products from the reaction of $(C_6H_5)_2PCl$ and $CH_3P(OCH_3)_2$ depended upon the initial molar ratio of the two reagents. Thus from 1 mol of each of the reagents at room temperature, the products are $(C_6H_5)_2P—P(O)(CH_3)(OCH_3)$ and CH_3Cl, as shown in eq. 1.

$$(C_6H_5)_2PCl + CH_3P(OCH_3)_2 \rightarrow (C_6H_5)_2P—P(O)(CH_3)OCH_3 + CH_3Cl \qquad (1)$$

However, when an excess of $(C_6H_5)_2PCl$ was present initially, the chlorophosphine further reacted with the diphosphine monoxide derivative to give $(C_6H_5)_2P—P(C_6H_5)_2$ and $CH_3P(O)(OCH_3)Cl$, according to eq. 2.

$$(C_6H_5)_2P—P(O)(CH_3)OCH_3 + (C_6H_5)_2PCl \rightarrow (C_6H_5)_2P—P(C_6H_5)_2 + CH_3P(O)(OCH_3)Cl \qquad (2)$$

While studying some reactions of dihalophenylarsines with trimethyl phosphite, we found [2] a reaction somewhat similar to the one shown in eq. 2 occurring between $C_6H_5AsI_2$ and $P(OCH_3)_3$, eq. 3 and 4.

$$C_6H_5AsI_2 + P(OCH_3)_3 \rightarrow C_6H_5As(I){-}P(O)(OCH_3)_2 + CH_3I \qquad (3)$$

$$C_6H_5As(I){-}P(O)(OCH_3)_2 + C_6H_5AsI_2 \rightarrow C_6H_5As(I){-}As(I)C_6H_5 + CH_3P(O)(OCH_3)I \qquad (4)$$

However, only one product, $C_6H_5As[P(O)(OCH_3)_2]_2$, was obtained from $C_6H_5AsCl_2$ and $P(OCH_3)_3$ irrespective of the initial reagent ratio. This was true even after keeping the mixture at room temperature for one month or heating at 80–90°C for 24 h. In other words, under our experimental conditions $P(OCH_3)_3$ did not reduce $C_6H_5AsCl_2$. These results prompted us to study the reducing property of $CH_3P(OCH_3)_2$ toward $C_6H_5AsCl_2$ and $(C_6H_5)_2AsCl$ as well as that of $P(OCH_3)_3$ towards $(C_6H_5)_2AsCl$. These results are presented in this report.

Experimental

All reactions were carried out in the absence of air and moisture by using procedures describing previously [2]. Nuclear magnetic resonance (NMR) experiments and referencing methods were also similar to the ones previously described [2].

Reagents

The dimethoxymethylphosphine, $CH_3P(OCH_3)_2$, was prepared according to the method of Maier [3]. Chlorodiphenylphosphine, $(C_6H_5)_2PCl$ (obtained from Strem Chemicals, Inc., Danvers, Mass.), and dichlorophenylarsine, $C_6H_5AsCl_2$ (purchased from Alfa Inorganics, Beverly, Mass.) were distilled prior to use. Dichloromethane CH_2Cl_2, which was of spectrograde quality was dried over P_2O_5 and distilled.

Preparation of $C_6H_5As[P(O)(CH_3)OCH_3]_2$

In a representative reaction 1.93 g (17.9 mmol) of $CH_3P(OCH_3)_2$ was mixed with 1.32 g (5.9 mmol) of $C_5H_5AsCl_2$ in 1 ml of CH_2Cl_2 in a sealed evacuated tube. Upon mixing the reagents at room temperature, an exothermic reaction occurred. After 1/2 h, all the volatile materials were removed in vacuum and $C_6H_5As[P(O)(CH_3)OCH_3]_2$ was obtained as a colorless, viscous liquid. The yield was essentially quantitative. The only impurity present was a small amount (<5%) of $(CH_3)_2P(O)OCH_3$ ($\delta(P)$ −51.5 ppm) produced by the rearrangement of $CH_3P(OCH_3)_2$. The structure of the major product has been established from its reactions with $(C_6H_5)_2PCl$ and C_6H_5AsCl and from its NMR spectra. NMR: Proton spectrum; $\delta(C_6H_5)$ 7.8, 7.3 ppm (multiplets); $\delta(OCH_3)$ 4 doublets at 3.60 (J(PH) 12.5 Hz), 3.55 (J(PH) 12 Hz), 3.45 (J(PH) 12 Hz) and 3.4 ppm (J(PH) 11.5 Hz); $\delta(CH_3)$, 4 doublets at 1.60 (J(PH) 14 Hz), 1.51 (J(PH) 12.5 Hz), 1.42 (J(PH) 12.5 Hz) and 1.35 ppm (J(PH) 13.5 Hz). Phosphorus spectrum $\{^1H\}$: −62.54 (doublet, J(PP) 5.9 Hz), −60.74, −60.43 (doublet, J(PP) 5.9 Hz) and −59.76 ppm. Anal. Found: C, 35.9; H, 4.7; As, 21.0; P, 17.2. $C_{10}H_{17}O_4P_2As$ calcd.: C, 35.5; H, 5.1; As, 22.2; O, 18.9; P, 18.3%.

Preparation of [$C_6H_5As]_6$

In a typical reaction, 0.29 g (2.7 mmol) of $CH_3P(OCH_3)_2$ was mixed with 0.91 g (4.08 mmol) of $C_6H_5AsCl_2$ in 0.5 ml of CH_2Cl_2 in a sealed tube. After 24 h at room temperature, a white solid was removed by filtration, washed with hexane, and dried in vacuo; m.p. 205—207°C (lit. [4] range of melting points for $(C_6H_5As)_6$ between 195 and 212). The $(C_6H_5As)_n$ structure of this compound was established by its conversion to $C_6H_5As(I)—As(I)C_6H_5$ [2] upon treatment with elemental iodine in benzene. The $^{31}P\{^1H\}$ spectrum of the filtrate after separating $(C_6H_5As)_n$ showed two resonances of ca. equal intensity at −23.5 and −23.8 ppm and a resonance at −40.8 due to $CH_3P(O)(OCH_3)Cl$ [1].

Similar results are obtained when pure $C_6H_5As[P(O)(CH_3)OCH_3]_2$ in CH_2Cl_2 is treated with a molar equivalent of $C_6H_5AsCl_2$.

Reaction of $C_6H_5As[P(O)(CH_3)OCH_3]_2$ with $(C_6H_5)_2PCl$

This reaction was carried out in a 5 mm NMR tube with weighted quantities of the reagents in the presence of CH_2Cl_2. The structure of the resulting product $(C_6H_5)_2P—P(O)(CH_3)OCH_3$ was established by comparison of its NMR spectrum with an authentic sample [1] prepared from $(C_6H_5)_2PCl$ and $CH_3P(OCH_3)_2$.

Preparation of $(C_6H_5)_2As—P(O)(OCH_3)_2$ and its reaction with $(C_6H_5)_2AsCl$

An amount of $(C_6H_5)_2AsCl$ weighing 0.97 g (3.6 mmol) was mixed with 0.6 g (4.8 mmol) of $P(OCH_3)_3$ in a sealed tube and kept at room temperature for 24 h. The volatiles were removed in vacuum to obtain $(C_6H_5)_2As—P(O)(OCH_3)_2$ as a colorless liquid. Its NMR spectra clearly establish the assigned structure: NMR: Proton spectrum: $\delta(C_6H_5)$ 7.85, 7.55 ppm (multiplets, 10 H), $\delta(OCH_3)$ 3.67 ppm (doublet, 6 H), $J(PH)$ 11.5 Hz. Phosphorus spectrum $\{^1H\}$: −34.6 ppm. The yield was essentially quantitative.

In an NMR tube, 0.51 g of $(C_6H_5)_2As—P(O)(OCH_3)_2$ was mixed with 0.43 g of C_6H_5AsCl and the tube was sealed after evacuation. There was no reaction after 2 weeks at room temperature or heating at about 80—90°C for 24 h as evidenced by NMR spectra.

Preparation of $(C_6H_5)_2As—P(O)(CH_3)(OCH_3)$ and its reaction with $(C_6H_5)_2AsCl$

The preparation of $(C_6H_5)_2As—P(O)(CH_3)(OCH_3)$ was carried out as described above with 0.65 g (2.45 mmol) of $(C_6H_5)_2AsCl$ and 0.82 g (7.6 mmol) of $CH_3P(OCH_3)_2$. $(C_6H_5)_2As—P(O)(CH_3)OCH_3$ was obtained as a viscous liquid. NMR: Proton spectrum $\delta(C_6H_5)$ 7.71, 7.39 ppm (multiplets, 10 H), $\delta(OCH_3)$ 3.71 ppm (doublet, 3 H) $J(PH)$ 12 Hz, $\delta(CH_3)$ 1.55 ppm (doublet, 3 H) $J(PH)$ 14 Hz. Phosphorus spectrum $\{^1H\}$: −60.8 ppm. The yield was quantitative.
In a glass tube 0.69 g (2.14 mmol) of $(C_6H_5)_2As—P(O)(CH_3)OCH_3$ was mixed with 0.9 g (3.6 mmol) of $(C_6H_5)_2AsCl$ in the presence of ca. 0.5 ml CH_2Cl_2. The mixture was heated at ~80° for 20 h. On cooling, colorless crystals separated. They were filtered, washed with hexane, and dried in vacuum; m.p. 120, 123°C (lit. [5] 120—125°C for $(C_6H_5)_2As—As(C_6H_5)_2$). The mass spectrum of this compound, recorded with direct introduction of the sample at an ionization voltage of 70 eV, showed a parent peak at 458 corresponding to the molecular weight of tetraphenyldiarsine. Anal.: Found C, 51.3; H, 5.4; As, 22.3; P, 9.0.

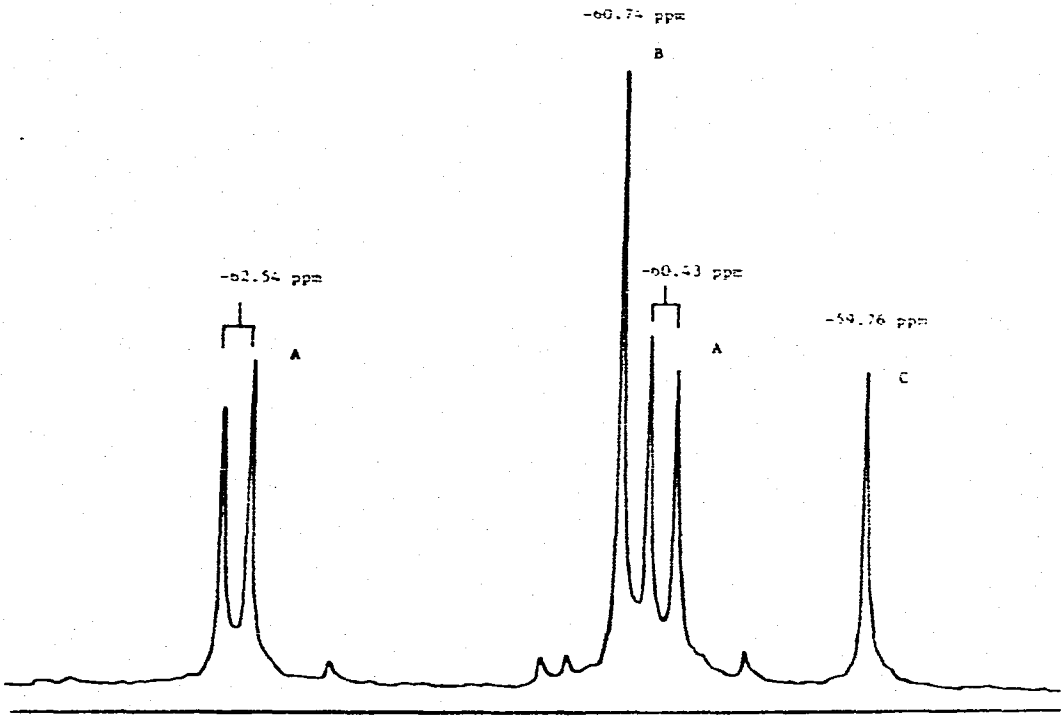


Fig. 1. The proton-decoupled ^{31}P NMR spectrum of $C_6H_5As[P(O)(CH_3)(OCH_3)]_2$ recorded at a sweep width of 500 Hz on a Varian XL-100-15 spectrometer in the Fourier-transform mode. The chemical shifts are reported from 85% H_3PO_4 at 0 ppm.

$C_{14}H_{16}O_2PAs$ calcd.: C, 52.2; H, 5.0; As, 23.3; P, 9.6%.

The NMR spectra of the filtrate from the separation of $(C_6H_5)_2As—As(C_6H_5)_2$ showed the presence of several products including $CH_3P(O)(OCH_3)Cl$.

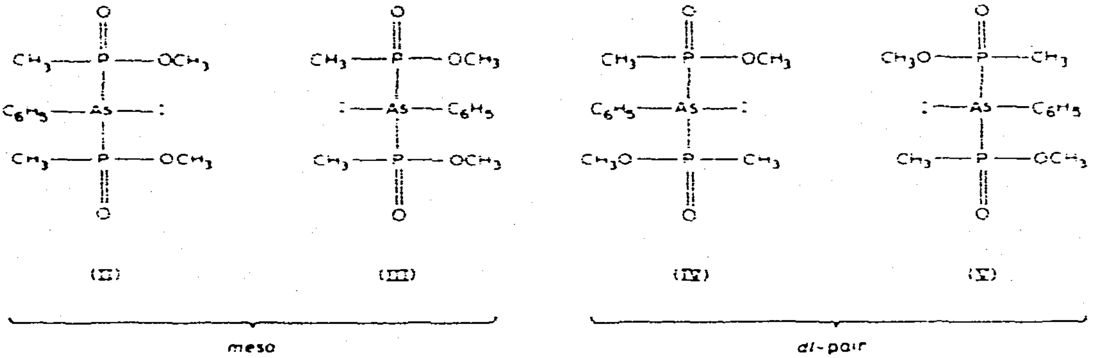
Results and discussion

When $C_6H_5AsCl_2$ (1 mol) is treated with an excess of $CH_3P(OCH_3)_2$ (> 2 mol) in CH_2Cl_2 at room temperature, an exothermic reaction (eq. 5) ensues with the liberation of 2 mol of chloromethane, as evidenced by quantitative ^1H NMR analysis in 12 mm NMR tubes filled nearly full of the reagent mixture and then sealed.

$$C_6H_5AsCl_2 + 2CH_3P(OCH_3)_2 \rightarrow \underset{(I)}{C_6H_5As[P(O)(CH_3)OCH_3]_2} + 2CH_3Cl \qquad (5)$$

The new compound I is obtained as a colorless liquid which is stable at room temperature in the absence of air, moisture, and excess of $C_6H_5AsCl_2$. In the previous paper [2], we have given spectral evidence to support the view that $C_6H_5As[P(O)(OCH_3)_2]_2$ prepared from $C_6H_5AsCl_2$ and $P(OCH_3)_3$, indeed contains As—P bonds rather than As—O—P linkages. The convincing evidence for this was the ^{31}P spectrum of I which showed a singlet at —30.9 ppm, a chemical shift value in the range found for quadruply connected phosphorus atoms. Because of the large quadrupolar interaction, ^{75}As did not show coupling with the phosphorus resonance.

The proton-decoupled ^{31}P NMR spectrum of I in CH_2Cl_2, reproduced as Fig. 1, shows six peaks between −63 and −58 ppm, two of which are singlets while the rest consist of a pair of doublets with a J value of 5.9 Hz. These chemical shifts are in agreement with structure I having direct As—P bonds since they compare very well with the chemical shift of −59.42 ppm for the $CH_3P(O)OCH_3$ moiety in $(C_6H_5)_2P{-}P(O)(CH_3)OCH_3$ [1]. The observed multiplets in Fig. 1 can be assigned to three diastereoisomers of I. Note that each phosphorus atom in I is an asymmetric center and the structure of I represents a case analogous to that of trihydroxyglutaric acid, $CH(OH)[CH(OH)COOH]_2$ [6].



(II) (III) (IV) (V)

meso *dl*-pair

The possible isomers of I (II—IV) are shown. IV and V are mirror images (*dl*-pair) and therefore would be expected to exhibit one set of resonance(s) in the NMR spectrum. However, the two phosphorus atoms in the *dl*-pair (IV and V) are not equivalent and the expected spectrum would consist of a pair of doublets. On this basis the pair of doublets marked A in Fig. 1 is assigned to the *dl*-pair. The *meso*-isomers, II and III should each exhibit a singlet since the two phosphorus atoms in each isomer are magnetically equivalent. The peaks designated B and C are therefore attributed to the two *meso*-isomers but they cannot be separately assigned. The proton NMR spectrum also shows the expected multiplicity in both the methyl and methoxyl regions. Since there are two kinds of methyl and methoxyl groups, the ^{31}P undecoupled ^{1}H spectrum of the *dl*-pair, upon good resolution, should exhibit a pair of doublets in the CH_3P as well as in the CH_3OP spectral regions. Each of the two *meso*-isomers should give rise to a doublet in the same spectral regions. The observed ^{1}H NMR spectrum of I in CH_2Cl_2 does show the eight peaks in the CH_3P as well as in the CH_3OP regions.

The justification for the assignment of the six resonances in the ^{31}P spectrum to the $CH_3P(O)(OCH_3)$ moieties of the 3 diastereoisomers of $C_6H_5As[P(O)(CH_3)OCH_3]_2$ comes from the reactions of the latter with $(C_6H_5)_2PCl$. Thus treatment of I with 2 molar equivalents of $(C_6H_5)_2PCl$ produces $(C_6H_5)_2P{-}P(O)(CH_3)OCH_3$ as shown in eq. 6. This reaction is quite fast at room temperature, being com-

$$C_6H_5As[P(O)(CH_3)OCH_3]_2 + 2(C_6H_5)_2PCl \rightarrow C_6H_5AsCl_2 + 2(C_6H_5)_2P{-}P(O)(CH_3)OCH_3 \qquad (6)$$

plete within fifteen minutes, at which time the first NMR spectrum of the reaction mixture was recorded. The ^{31}P NMR spectrum of the reaction products showed that all the six ^{31}P resonances in Fig. 1 disappeared and the spectrum was identical to that found [2] for $(C_6H_5)_2P{-}P(O)(CH_3)OCH_3$ prepared from $(C_6H_5)_2PCl$ and $CH_3P(OCH_3)_2$. It should be pointed out that we had observed [2] a similar reaction between $(C_6H_5)_2PCl$ and $C_6H_5As[P(O)(OCH_3)_2]_2$ to give $C_6H_5AsCl_2$ and $(C_6H_5)_2P{-}P(O)(OCH_3)_2$. This reaction of I is evidence that the six peaks in the ^{31}P spectrum are all due to the $CH_3P(O)(OCH_3)$ moiety and that the multiplicity in the spectrum may be assigned to the presence of the diastereoisomers.

When $C_6H_5As[P(O)(CH_3)OCH_3]_2$ is treated with an excess of $C_6H_5AsCl_2$ or when $C_6H_5AsCl_2$ and $CH_3P(OCH_3)_2$ are combined in a molar ratio of ca. 2 : 1, arsenobenzene, $[C_6H_5As]_6$, is produced in about 6 h. Note that this reaction is analogous to the ones shown in eq. 2 and 4. The phosphorus moiety in I is converted to $CH_3P(O)(OCH_3)Cl$ and other products found [1] in the reaction between excess $(C_6H_5)_2PCl$ and $CH_3P(OCH_3)_2$. Under similar experimental conditions or on heating to about 90°C, there was no reaction between $C_6H_5AsCl_2$ and $C_6H_5As[P(O)(OCH_3)_2]_2$.

Because of this difference in reactivity of $C_6H_5AsCl_2$ towards the two methoxyphosphines, we thought it desirable to examine the reactions of $(C_6H_5)_2AsCl$ with either $P(OCH_3)_3$ or $CH_3P(OCH_3)_2$. With 1 mol of $(C_6H_5)_2AsCl$ and 1 mol of either $CH_3P(OCH_3)_2$ or $P(OCH_3)_3$, the products are $(C_6H_5)_2As{-}P(O)(CH_3)OCH_3$ and $(C_6H_5)_2As{-}P(O)(OCH_3)_2$, respectively. As with I, the new compound $(C_6H_5)_2As{-}P(O)(CH_3)(OCH_3)$ reacts with another mol of $(C_6H_5)_2AsCl$ to produce $(C_6H_5)_2As{-}As(C_6H_5)_2$. This reaction can also be carried out in one step with 2 mol of $(C_6H_5)_2AsCl$ and 1 mol of $CH_3P(OCH_3)_2$. However, under the experimental conditions employed in this study, there was no reaction between $(C_6H_5)_2As{-}P(O)(OCH_3)_2$ and $(C_6H_5)_2AsCl$.

It may be interesting to speculate on the differences in reactivity of $(C_6H_5)_2AsCl$ or $C_6H_5AsCl_2$ towards the two methoxyphosphines, $CH_3P(OCH_3)_2$ and $P(OCH_3)_3$, when the chloroarsines are present in excess. If it is assumed that an onium intermediate VI, as shown in eq. 7, is involved in the formation of the As—As bond from an As—P bond and an As—Cl bond, then this intermediate

$$(C_6H_5)_2As{-}P(O)(CH_3)(OCH_3) + (C_6H_5)_2AsCl \rightarrow$$

$$\underset{(VI)}{([(C_6H_5)_2As{-}\overset{+}{A}s(C_6H_5)_2{-}P(O)(CH_3)OCH_3]Cl^-} \rightarrow$$

$$(C_6H_5)_2As{-}As(C_6H_5)_2 + CH_3P(O)(OCH_3)Cl \qquad (7)$$

ought to be stabilized by a higher electron density at the As—P bond. Thus the methyl group by releasing electrons favors the formation of this type of an intermediate and hence the completion of reaction 7, while the electron-withdrawing methoxyl group does not.

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