Reactions of Calcium Carbide. A Novel Synthesis of Tetraphenyldiphosphine and Diphenylphosphinic Anhydride

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Abstract: Calcium carbide, functioning as a reducing agent, reacts with diphenylchlorophosphine to give tetraphenyldiphosphine under mild conditions. Oxidation of the tetraphenyldiphosphine with oxygen has been reported to give quantitative yields of the corresponding mono- or dioxide. If the oxidation is carried out in the presence of diphenylchlorophosphine, excellent yields of diphenylphosphinic anhydride are obtained. A mechanism is proposed to account for all products.

In an earlier communication, we reported a novel synthesis of tetraphenyldiphosphine,[1] $(C_6H_5)_2P-P(C_6H_5)_2$, where diphenylchlorophosphine, $(C_6H_5)_2PCl$, was found to undergo smooth reaction with calcium carbide forming tetraphenyldiphosphine, calcium chloride, and elemental carbon. The tetraphenyldiphosphine was identified by its infrared spectrum[2,3] and melting point.

To further substantiate the presence of the compound, two derivatives were prepared. Reaction with oxygen gave tetraphenyldiphosphine dioxide, $(C_6H_5)_2P(O)P(O)(C_6H_5)_2$, while reaction with sulfur yielded tetraphenyldiphosphine disulfide, $(C_6H_5)_2P(S)P(S)(C_6H_5)_2$. Both the dioxide and disulfide were identified by their infrared spectra,[2] melting points,[2] and mass spectra.

The reaction of calcium carbide with diphenychlorophosphine is apparently an oxidation–reduction reaction in which calcium carbide functions as a reducing agent. Similar reactions of calcium carbide are known in that it is reported to reduce metal chlorides, oxides, etc., to the corresponding metal;[4,5] however, all reported reductions require high temperatures, 700–1000°. The reaction conditions we reported, 100–150°, appear to be unique in the light of the earlier work.

In the isolation of tetraphenyldiphosphine, several other compounds were observed if air was not rigorously excluded. Tetraphenyldiphosphine mono- and dioxide were isolated and could be readily explained *via* air oxidation of the primary product, tetraphenyldiphosphine. However, most unexpectedly, diphenylphosphinic anhydride, $(C_6H_5)_2P(O)OP(O)(C_6H_5)_2$, was also observed, the presence of which could not be explained.

Tetraphenyldiphosphine has been synthesized by several more conventional routes, which have been discussed by Cowley[6] and Huheey.[7]

Various routes to diphenylphosphinic anhydride have also been reported. These methods include the reaction of diphenylchlorophosphine oxide with the sodium salt of diphenylphosphinic acid[8] and the reaction of ethyl diphenylphosphinite and diphenylphosphine oxide with diphenylchlorophosphine oxide[9] in the presence of a tertiary amine. Other methods involve the action of paraformaldehyde on diphenylchlorophosphine oxide[10] and the reaction of alkyl esters of diphenylphosphinic acid with *gem* dihalides.[11]

Discussion

Formation of tetraphenyldiphosphine is presumed to be an oxidation–reduction reaction with calcium carbide functioning as a reducing agent. This is evidenced by the formation of a stoichiometric amount of elemental carbon.

It is conceivable that diphenylchlorophosphine is reduced to free radical intermediate species which subsequently combine to form the observed tetraphenyldiphosphine.

$$CaC_2 + 2(C_6H_5)_2PCl \longrightarrow 2(C_6H_5)_2P\cdot + 2C + CaCl_2 \quad (1)$$

$$2(C_6H_5)_2P\cdot \longrightarrow (C_6H_5)_2PP(C_6H_5)_2 \quad (2)$$

Since radicals have been reported to combine with scavengers such as sulfur[12] an attempt was made to block the formation of the P–P bond by carrying out the reaction in the presence of sulfur. If free radicals existed as intermediates the scavenger would result in compounds not containing the P–P linkage. The formation of these new compounds would serve to reduce or completely prevent the formation of tetraphenyldiphosphine.

It was found that when the reaction was carried out in the presence of sulfur, at 110°, no tetraphenyldiphosphine was formed. In order to establish that the reaction which occurred did not involve the initial formation of tetraphenyldiphosphine which subsequently treated with sulfur, comparable experiments were conducted in which authentic tetraphenyldiphosphine was treated with sulfur both in the absence and presence of diphenylchlorophosphine. The latter experiments resulted in the formation of tetraphenyldiphosphine disulfide. These reactions are shown below.

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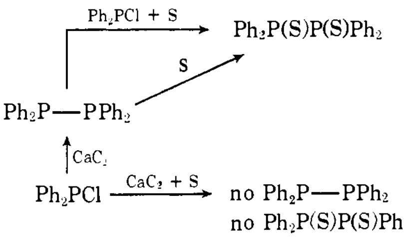


The inhibiting effect of sulfur on the formation of the phosphorus-phosphorus bond is interpreted to indicate that the formation of tetraphenyldiphosphine proceeds *via* a free radical intermediate, which in the presence of elemental sulfur was scavenged, thus preventing the formation of the tetraphenyldiphosphine. While this datum is consistent with a free radical intermediate, it is not conclusive and the system is under further study.

It was found that if oxygen was introduced into the reaction system prior to isolation of the tetraphenyldiphosphine, several oxygenated products were formed: tetraphenyldiphosphine monoxide, $(C_6H_5)_2P(O)P(C_6H_5)_2$; tetraphenyldiphosphine dioxide, $(C_6H_5)_2P(O)P(O)(C_6H_5)_2$, and diphenylphosphinic anhydride, $(C_6H_5)_2P(O)OP(O)(C_6H_5)_2$. If the reaction was run to completion, where all the CaC_2 was consumed, and then treated with hot toluene and centrifuged, several apparently different routes were open. If the toluene solution was evaporated in the absence of air, tetraphenyldiphosphine was isolated. If dry oxygen was introduced immediately into the toluene solution, the primary product was diphenylphosphinic anhydride with small amounts of tetraphenyldiphosphine dioxide. On the other hand, if oxygen was added very slowly to the toluene solution while stirring, the primary product was the dioxide with small amounts of anhydride. These observations might suggest that a long-lived radical was present; however, study of the system by esr gave no support to such a hypothesis.

In order to obtain additional information concerning a possible mechanism for the formation of diphenylphosphinic anhydride, a number of other experiments were carried out. Tetraphenyldiphosphine, carefully purified to remove traces of diphenylchlorophosphine, was dissolved in toluene and allowed to react with oxygen. This reaction resulted in the formation of only tetraphenyldiphosphine dioxide. On the other hand, if diphenylchlorophosphine was introduced, even in small amounts, the reaction of tetraphenyldiphosphine in the presence of oxygen resulted in the formation of diphenylphosphinic anhydride.

$$2(C_6H_5)_2PP(C_6H_5)_2 + 3O_2 \xrightarrow{(C_6H_5)_2PCl} 2(C_6H_5)_2P(O)OP(O)(C_6H_5)_2 \quad (3)$$

Under similar conditions, it was found that the monoxide in the presence of diphenylchlorophosphine could also be converted to the anhydride (reaction 4).

$$(C_6H_5)_2P(O)P(C_6H_5)_2 + O_2 \xrightarrow{(C_6H_5)_2PCl} (C_6H_5)_2P(O)OP(O)(C_6H_5)_2 \quad (4)$$

However, not unexpectedly, there was no reaction with the dioxide. It was also established that tetraphenyldiphosphine monoxide on reaction with oxygen in the absence of diphenylchlorophosphine yielded only the dioxide.

$$(C_6H_5)_2P(O)P(C_6H_5)_2 + {}^1/_2O_2 \longrightarrow (C_6H_5)_2P(O)P(O)(C_6H_5)_2 \quad (5)$$

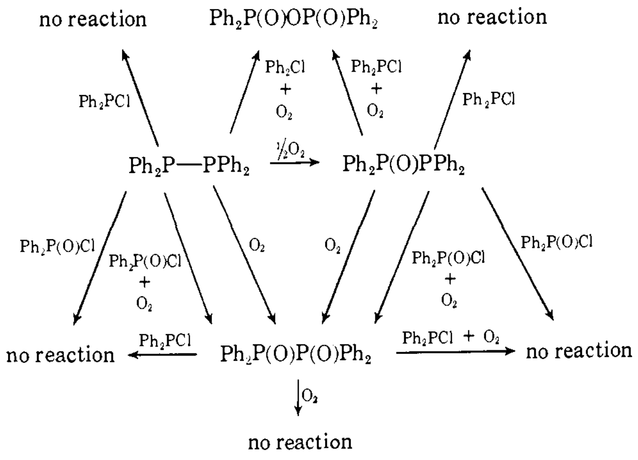
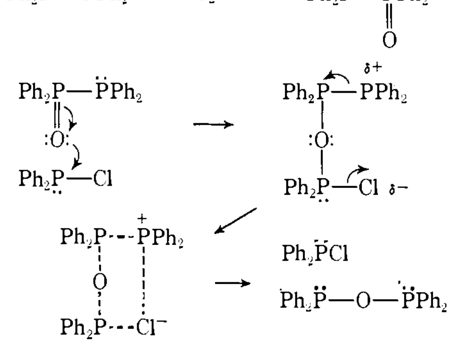


Figure 1. Reactions evaluated in the formation of diphenylphosphinic anhydride.

It is quite apparent that the diphenylchlorophosphine or some related species plays a significant role in the oxidation of the diphosphine to the anhydride. Colloidal carbon, which was most likely never completely removed, may also be important in the reaction; however, there is no evidence to support this thought particularly since all the reactions can be duplicated using commercial tetraphenyldiphosphine.

Diphenylchlorophosphine oxide, $(C_6H_5)_2P(O)Cl$, could be considered as a possible oxygenating agent in that at the end of the reaction a liquid product was observed which clearly showed major bands at 1443, 1236, and 521 cm^{-1}. These bands were associated with P—C, P=O, and P—Cl, respectively, in the compound diphenylchlorophosphine oxide.[13] (Comparison with the spectrum of an authentic sample confirmed the existence of the oxide.) However, no anhydride was formed in the reaction of oxygen and authentic diphenylchlorophosphine oxide with tetraphenyldiphosphine or the monoxide. These and other related reactions are summarized in Figure 1. Thus it is suggested that the initial step in the reaction involves the formation of tetraphenyldiphosphine monoxide, which results from reaction of tetraphenyldiphosphine with oxygen. The reaction then proceeds through electrophilic attack on the phosphoryl oxygen of the monoxide followed by nucleophilic attack at the nonoxygenated phosphorus of the tetraphenyldiphosphine monoxide by Cl$^-$, as outlined below, to form diphosphoxane, $(C_6H_5)_2POP(C_6H_5)_2$, and diphenylchlorophos-



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phine. Electrophilic attack on the phosphoryl oxygen has been suggested in the reaction of phosphinic acid esters with acid chlorides[14] and thus it is not unreasonable to expect a similar attack in this reaction to form anhydride.

On rapid, continued addition of oxygen, the ether-type intermediate undergoes further oxidation to diphenylphosphinic anhydride.

$$\mathrm{Ph_2POPPh_2 + O_2 \longrightarrow Ph_2P(O)OP(O)Ph_2} \qquad (6)$$

On the other hand, if oxygen is added slowly the ether-type intermediate, diphosphoxane [$\mathrm{Ph_2POPPh_2}$], undergoes rearrangement

$$\mathrm{Ph_2POPPh_2 \longrightarrow Ph_2P(O)PPh_2} \qquad (7)$$

in the Arbuzov manner to the monoxide.[15]

In this reaction system, the diphosphoxane undergoes reaction to form the anhydride or rearranges to the monoxide. It should be noted that the rearrangement product, tetraphenyldiphosphine monoxide, can be recycled and still lead to the anhydride. The important step in the reaction sequence appears to be the availability of oxygen to rapidly trap the ether intermediate in the oxidized, anhydride, form.

It appears unlikely that tetraphenyldiphosphine monoxide functions as the oxygenating agent in anhydride formation since it is completely converted to dioxide in the absence of diphenylchlorophosphine. Some anhydride, however small, would be expected if the monoxide played any role as an oxygenating agent.

This reaction appears to be the most convenient route presently available for the formation of diphenylphosphinic anhydride.

Experimental Section

Diphenylchlorophosphine (Alfa Inorganics, Inc., Beverly, Mass.) was vacuum distilled and the fraction boiling at 134-136° (2-2.5 mm), refractive index $n^{21.6}\mathrm{D}$ 1.6364, was used. Either powdered calcium carbide of 99.9% purity (Research Inorganics Chemical Co., Sun Valley, Calif.) or commercial material of 85% purity was used. The commercial material was ground in a vibrating ball mill and the particles passing through a 60-mesh screen were used. No difference in reactivity or product distribution was noted between the commercial and high-purity calcium carbide.

Reagent grade toluene was dried over sodium and distilled prior to use. Other solvents, either spectroquality or reagent grade, were deaerated with argon prior to use.

Reactions were carried out in an all-glass apparatus connected to a conventional glass high-vacuum system, which is described elsewhere.[16,17] Dow Corning high-vacuum grease was used on all joints which were near heated areas. Apiezon "N" grease was used on all other joints and stopcocks.

All glassware was dried before use. Additions of reagents were made under an atmosphere of either argon or nitrogen. In all cases, rigorous precautions were taken to exclude moisture and air. Melting points were obtained in vacuum sealed capillaries and are uncorrected. Analyses were performed by the FMC Corporation, Princeton, N. J., and the Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Infrared spectra were determined as KBr pellets and nmr spectra (Varian A-60A) were run in $\mathrm{CDCl_3}$ solution with tetramethylsilane as an internal standard. Electron spin resonance spectra were obtained using the Varian Model V-4500-10 esr control unit with a V-4500-40 X-band microwave bridge. Mass spectra were obtained with a Consolidated Electrodynamics 21-110 HR mass spectrometer using an ionization potential of 70 eV and a direct probe inlet temperature of 200°. Molecular weights were obtained from the parent ion in the mass spectral fragmentation pattern.

Tetraphenyldiphosphine, $\mathrm{(C_6H_5)_2PP(C_6H_5)_2}$. A typical procedure is given in detail for tetraphenyldiphosphine. Other derivatives were prepared by variations made during product isolation. Diphenylchlorophosphine, 3.3 g (15.0 mmol), was added to calcium carbide, 0.32 g (5.0 mmol), under an inert atmosphere. On mixing, trace amounts of acetylene, identified by infrared[18] and mass spectral analyses, were formed. Acetylene probably formed through reaction of calcium carbide with traces of moisture in the system. This reaction was allowed to continue at room temperature, with pumping, until no further evidence of gas evolution was observed. Acetylene product seldom consumed more than 2-3% of the initial calcium carbide. The mixture was then heated *in vacuo* to 150° with stirring for 16-20 hr. Almost immediately the mixture was observed to darken through formation of elemental carbon. Upon completion of the reaction, based on complete consumption of the calcium carbide, the mixture was cooled to room temperature, 25 ml of toluene added and the system heated to 100-105° to dissolve the tetraphenyldiphosphine. While hot, the mixture was centrifuged and the supernate filtered through decolorizing charcoal. Toluene was removed by evaporation under vacuum, leaving crude tetraphenyldiphosphine and unreacted diphenylchlorophosphine. The tetraphenyldiphosphine, dissolved in starting material, was precipitated by addition of dry ether, and the resulting solids were washed repeatedly with 5-ml portions of cold ether to remove unreacted diphenylchlorophosphine. The solid tetraphenyldiphosphine was then vacuum dried at room temperature. The exclusion of air and moisture from the system was necessary to prevent side reactions. Air (oxygen) caused the formation of tetraphenyldiphosphine mono- and dioxides, and/or diphenylphosphinic anhydride, while moisture led to partial conversion of diphosphine to diphenylphosphinic acid, $\mathrm{(C_6H_5)_2P(O)OH}$. Diphenylphosphinic acid was identified by its melting point (192-193°, lit.[2] 191-192°), infrared spectrum,[19] and chemical analysis. The acid, if formed, was removed by careful washing with deaerated 1% aqueous potassium hydroxide, followed by rapid rinsing with cold deaerated distilled water and ether and vacuum drying.

The tetraphenyldiphosphine melted at 118-119° (lit.[2] 120.5°). The infrared spectrum of tetraphenyldiphosphine was in good agreement with that reported,[2,3] but did indicate the presence of small amounts of tetraphenyldiphosphine dioxide.

The carbon formed in the reaction is quite active, rapidly picking up air and moisture. It gives a narrow fine-line esr spectrum at room temperature, with a g value of 2.002 ± 0.002. This is in good agreement with that reported for activated carbon.[20]

Reaction in the Presence of Sulfur. The reaction was carried out as indicated above, with the exception that sulfur was added to the diphenylchlorophosphine-calcium carbide mixture. Product isolation, also as described above, showed that the reaction system contained no tetraphenyldiphosphine or related species.

Tetraphenyldiphosphine Dioxide, $\mathrm{(C_6H_5)_2P(O)P(O)(C_6H_5)_2}$. Tetraphenyldiphosphine from the above preparation, washed free of diphenylchlorophosphine, was added to 25 ml of toluene. Dry oxygen in excess was introduced into the solution at room temperature over a period of 6 hr causing formation of tetraphenyldiphosphine dioxide. The toluene solution was then filtered through decolorizing charcoal and concentrated to the point of incipient crystallization by evaporation under vacuum. Upon standing crystals of tetraphenyldiphosphine dioxide formed, which were purified by recrystallization from toluene-ether. If moisture was inadvertently introduced during recrystallization, diphenylphosphinic acid formed and was removed by washing with 5% aqueous potassium hydroxide and drying as described previously.

Yields of tetraphenyldiphosphine dioxide were variable, ranging up to 50%, based on quantity of calcium carbide consumed, and 100% based on quantity of tetraphenyldiphosphine.

Tetraphenyldiphosphine dioxide melted at 168-169° (lit.[2] 169°) and had an infrared spectrum[2] identical with that reported. The mass spectrum exhibited a parent ion peak at 402 [$\mathrm{(C_6H_5)_2P(O)P(O)(C_6H_5)_2}$, mol wt 402] and a fragmentation pattern consistent with tetraphenyldiphosphine dioxide.

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Tetraphenyldiphosphine Disulfide, $(C_6H_5)_2P(S)P(S)(C_6H_5)_2$. Tetraphenyldiphosphine, from the initial preparation, was added to 25 ml of toluene containing sufficient sulfur for complete reaction. The mixture was heated to 100–105° with stirring, under an inert atmosphere for 6 hr. The hot toluene solution was then filtered and evaporated. This reaction resulted in essentially 100% conversion based on the initial quantity of tetraphenyldiphosphine. The white crystals obtained from this reaction were recrystallized from chloroform–methanol and vacuum dried. The infrared spectrum[2,3] was identical with that reported for tetraphenyldiphosphine disulfide. The mass spectrum was consistent, exhibiting a peak at 434, attributable to the parent ion [$(C_6H_5)_2P(S)P(S)(C_6H_5)_2$, mol wt 434].

Diphenylphosphinic Anhydride, $(C_6H_5)_2P(O)OP(O)(C_6H_5)_2$. Tetraphenyldiphosphine, 0.22 g (0.6 mmol) from the initial preparation, was added to 15 ml of toluene containing a small amount of diphenylchlorophosphine (0.05 g). Dry oxygen in excess was introduced into the solution at room temperature, and the reaction continued until oxygen take-up ceased. The toluene solution was then filtered through decolorizing charcoal, concentrated by evaporation under vacuum, and allowed to stand at room temperature. The crystals which formed on standing were washed repeatedly with dry, cold heptane or ether and dried under vacuum at room temperature. The material was then recrystallized several times from toluene. In this preparation as in those above, the presence of moisture led to the formation of diphenylphosphinic acid, which was removed by washing with 1% aqueous potassium hydroxide as described previously.

Diphenylphosphinic anhydride melted at 144–145°, lit.[10] 142–143°. Its infrared spectrum contained a band at 1236 cm^{-1} assigned to the P=O[21] stretching frequency and a band at 960 cm^{-1} assigned to the P—O—P[22] linkage.

Mass spectral data showed a parent ion peak corresponding to a mass of 418 [$(C_6H_5)_2P(O)OP(O)(C_6H_5)_2$; mol wt 418], and a fragmentation pattern consistent with that of diphenylphosphinic anhydride.

Anal. Calcd for $C_{24}H_{20}O_3P_2$: C, 68.90; H, 4.82; P, 14.81; O, 11.47. Found: C, 68.65; H, 4.66; P, 14.71; O, 11.96.

This reaction results in virtually complete conversion of the tetraphenyldiphosphine, forming a mixture containing more than 95% anhydride and less than 5% tetraphenyldiphosphine dioxide.

Diphenylphosphinic anhydride was produced in an identical manner using tetraphenyldiphosphine monoxide instead of the tetraphenyldiphosphine as starting material.

Diphenylphosphinic anhydride was also produced by adding oxygen directly to the cooled reaction mixture from the initial tetraphenyldiphosphine preparation, without first actually isolating the tetraphenyldiphosphine. Isolation and purification of the product were carried out as described previously. Yields based on calcium carbide consumed were about 40%.

In all of the procedures described, product yields were approximately 40%. These yields could be substantially improved by complete recovery of product retained on the inorganic salts and carbon.

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The Preparation and Characterization of 1-Germa-, 1-Stanna-, and 1-Plumba-2,3-dicarba-*closo*-dodecaborane(11)

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Abstract: Treatment of (3)-1,2-$B_9C_2H_{11}^{2-}$ with carbenoid germanium, tin, and lead reagents leads to the formation of icosahedral tricarbaborane analogs, $MC_2B_9H_{11}$ (M = Ge, Sn, Pb). The characterization of these new carbametallic boranes gives no evidence for substituents pendent from the metal. Facile removal of the metal is effected by treatment with methanolic KOH.

Extension of the known isoelectronic series of the icosahedral species $(B_{12}H_{12})^{2-}$, $(B_{11}CH_{12})^-$, and $B_{10}C_2H_{12}$ yields the unknown tricarbaborane $[B_9C_3H_{12}]^+$. The latter cation, owing to the characteristic electronegativity of neutral polyhedral carboranes,[1] would probably be acidic or perhaps even exist as the neutral $B_9C_3H_{11}$ molecule.

Results and Discussion

We have isolated carbametallic boranes[2] analogous to $B_9C_3H_{11}$ in that a carbon atom is replaced by another main group IV element, $MC_2B_9H_{11}$ (M = Ge, Sn, Pb). These carbametallic boranes, 1-germa-, 1-stanna-, and 1-plumba-2,3-dicarba-*closo*-dodecaborane(11), are formed from carbenoid reagents according to

$$(3)\text{-}1,2\text{-}B_9C_2H_{11}^{2-} + MX_2 \longrightarrow MB_9C_2H_{11} + 2X^- \quad (1)$$
$$(M = Ge, Sn, Pb)$$

The formation of $MC_2B_9H_{11}$ species by using $:MCl_2$ reagents to insert a metal atom into the vacant icosahedral position of the (3)-1,2-$B_9C_2H_{11}^{2-}$ ion[3] renders the reaction similar to that described by Hawthorne and Wegner[4] for the insertion of RB with $RBCl_2$ reagents. Todd, *et al.*,[5] describe another parallel in the formation of $B_{10}H_{10}CHP$ by treatment of $(B_{10}H_{10}CH)^{3-}$ with

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