Some New Reactions of Functions Containing Secondary Phosphorus[1]

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Received October 5, 1965

The following new reactions, all involving functional groups with a secondary phosphorus atom, have been observed. (1) Diarylphosphinous chlorides in the presence of a tertiary amine give tetraaryldiphosphine dioxides on exposure to oxygen and water. (2) Ethyl diphenylphosphinite reacts with diphenylphosphinic chloride to form diphenylphosphinic diphenylphosphinous anhydride. (3) The same anhydride is formed from reaction of diphenylphosphine oxide with diphenylphosphinic chloride in the presence of a tertiary amine. (4) Dibenzylphosphine oxide follows a different path with diphenylphosphinic chloride and is converted to a diphosphine derivative apparently by intermolecular dehydration. (5) Dialkylphosphine oxides can be converted smoothly to dialkylphosphinous chlorides by phosphorus trichloride.

We recently reported[3] that tetraphenyldiphosphine dioxide appeared as a by-product accompanying phosphinites in the reaction of diphenylphosphinous chloride with alcohols and a tertiary amine. The origin of this unusual by-product was puzzling; no reactions were known which could account for it. We have now identified a possible source of the by-product and have discovered that the reactions involved have value as a new synthetic route to tetraaryldiphosphine dioxides.[4] Some other new reactions of compounds having a secondary phosphorus atom have been discovered and are also described in this report.

An over-all expression for a reaction providing a diphosphine dioxide from a phosphinous chloride, under conditions of ester synthesis, was considered to be eq 1, which accounts satisfactorily for the change

$$\begin{array}{ccccc} 2Ar_2PCl + {}^1\!/_2O_2 & & & & \\ + & & & & \\ ROH + R'_3N & & RCl + R'_3NHCl & & \\ \text{or} & \longrightarrow & \text{or} & + Ar_2P(O)P(O)Ar_2 & (1) \\ H_2O + 2R'_3N & & 2R'_3NHCl & & \end{array}$$

in oxidation state. Several steps, in various sequences, are possible, and model systems were set up to examine some of them. We first showed that diphenylphosphine oxide and diphenylphosphinic chloride, likely contaminants in the phosphinous chloride from hydrolysis and oxidation, respectively, combine to give an entirely different product when mixed under similar reaction conditions (section C). The same product was formed from an alkyl diphenylphosphinate and diphenylphosphinic chloride (section B). Oxidative coupling of diphenylphosphine oxide was eliminated as a possibility when no diphosphine dioxide was formed on air oxidation of the oxide in an ether–tertiary amine mixture. We then found that alcohol was not necessary for the formation of the diphosphine dioxide; indeed, much higher yields were obtained in its absence, since it competed for the phosphinous chloride in ester synthesis. It then appeared that the formation of a diphosphine dioxide during the ester synthesis[3] could be attributed simply to inadvertent admittance of oxygen and water, and, when the reaction was carried out with ready access of these materials, high yields of the diphosphine dioxide resulted. The nature of this process is discussed further in section A.

A. New Synthesis of Tetrasubstituted Diphosphine Dioxides.—No reaction occurred when an ether solution of equimolar amounts of diphenylphosphinous chloride and diethylaniline was stirred with careful exclusion of air. However, on exposure to the atmosphere, a white precipitate formed. A water wash removed amine hydrochloride from this precipitate and left an insoluble residue identified by its melting point of 167–169° and infrared spectrum[5] as tetraphenyldiphosphine dioxide. More of this compound was recovered from the original ether solution. To expedite the hydrolysis and oxidation steps, the reaction was repeated in the presence of added water (about 1 equiv), with air being drawn over the solution. A total yield of tetraphenyldiphosphine dioxide of 79.4% resulted. Larger amounts of water were detrimental and caused hydrolysis of the phosphinous chloride to the secondary phosphine oxide. The reaction was successfully conducted in benzene or tetrahydrofuran solution, as well as with triethylamine as the base, but no product formed in the absence of a base. Occasionally the crude product had a low melting point but gave the expected infrared spectrum. This may be due to the presence of some tetraphenyldiphosphine monoxide, which has been reported[6] to melt at 155–158° and to have an infrared spectrum very similar to that of the dioxide.

The nature of the step in which the P–P bond is formed is of interest, but remains uncertain. Originally, we suggested[4] that an intermediate ($Ar_2P\text{–}\overset{+}{P}Ar_2Cl$) might be formed by amine-catalyzed self-condensation of the phosphinous chloride and that hydrolysis and oxidation steps then followed. Placing diphenylphosphine oxide or diphenylphosphinic chloride in the reaction mixture had no influence on the yield of the diphosphine dioxide, supporting the idea of P–P bond formation preceding the hydrolysis and oxidation steps. Also, as discussed in section C, a combination of these compounds gave a product of O-phosphinylation, $(C_6H_5)_2P\text{–}O\text{–}P(O)(C_6H_5)_2$ (I). In the first experiment[4] testing the involvement of diphenylphosphine oxide, this compound was added to a typical reaction mixture after all other ingredients. However, in a later experiment, the oxide was placed in ether and triethylamine and the mixture was then treated with the phosphinous chloride. Whereas no water was intentionally added, experience has indicated the difficulty of preventing these systems

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(1) From the Ph.D. Dissertation of H. G. Anderson, Duke University, 1965. This investigation was supported in part by Public Health Service Research Grant No. CA-05507-04 from the National Cancer Institute.

(2) Philip Morris Research Assistant, 1962–1964.

(3) L. D. Quin and H. G. Anderson, *J. Org. Chem.*, **29**, 1859 (1964).

(4) Preliminary communication: L. D. Quin and H. G. Anderson, *J. Am. Chem. Soc.*, **86**, 2090 (1964).

(5) W. Kuchen and H. Buchwald, *Ber.*, **91**, 2871 (1958).

(6) J. KcKechnie, D. S. Payne, and W. Sim, *J. Chem. Soc.*, 3500 (1965).

TABLE I

DIPHOSPHINE DIOXIDES FROM PHOSPHINOUS CHLORIDES

$R_1R_2P(O)P(O)R_1R_2$					Carbon, %		Hydrogen, %		Phosphorus, %	
R_1	R_2	Mp, °C	Yield, %	Formula	Calcd	Found	Calcd	Found	Calcd	Found
C_6H_5	C_6H_5	167–169[a]	79	$C_{24}H_{20}O_2P_2$	71.64	71.37	5.01	4.93	15.40	15.18
p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	165–168[b]	54	$C_{28}H_{28}O_2P_2$	73.35	73.58	6.16	6.09	13.51	13.61
C_6H_5	p-ClC_6H_4	155–156	63	$C_{24}H_{18}Cl_2O_2P_2$	61.16	61.45	3.85	3.93	13.15	12.99
C_6H_5	p-CNC_6H_4	180–182	56	$C_{26}H_{18}N_2O_2P_2$	69.01	69.10	4.01	4.19	13.69	13.70
$C_6H_5CH_2$	$C_6H_5CH_2$	158–159	56	$C_{28}H_{28}O_2P_2$	73.35	73.36	6.16	5.92	13.51	13.48

[a] Lit.[5] mp 167°. [b] Lit.[20] mp 159–163°. Recrystallization of this sample raised the melting point to 183–185° with no change in the infrared spectrum.

from acquiring trace, but still significant, amounts. The water-insoluble reaction product was found by infrared analysis to be a mixture of tetraphenyldiphosphine dioxide and acid anhydride I or diphenylphosphinic anhydride (the spectrum did not permit distinction of these) in the approximate ratio 5:2. As noted above, the most obvious reaction giving an anhydride would be that between the secondary oxide and diphenylphosphinic chloride, the latter arising from oxidation of some of the phosphinous chloride. Assuming then that at least half of the phosphorus of the anhydride originates from the phosphinous chloride, the maximum yield of diphosphine dioxide obtainable from the remainder of the phosphinous chloride through inadvertent entry of water in this experiment would be 8.5 g. In fact, the yield was 11 g, and to have formed this amount a 100% yield from the *total* phosphinous chloride would have been required. It thus appears that some of the diphosphine dioxide might have originated from the reaction shown by eq 2. However, in the typical diphosphine dioxide

$$(C_6H_5)_2P(O)H + (C_6H_5)_2PCl \xrightarrow[O_2]{\text{base}} (C_6H_5)_2P(O)P(O)(C_6H_5)_2 \quad (2)$$

syntheses, I has not been observed as a by-product. Furthermore, when another secondary oxide, (p-chlorophenyl)phenylphosphine oxide, was tried under the same conditions with diphenylphosphinous chloride, no diphosphine dioxide or anhydride resulted. In view of these conflicting observations, it is not possible to specify the sequence of events in the diphosphine dioxide synthesis, and further study is necessary.

Two related reactions have been described recently. Sisler and co-workers[7] have observed formation of tetraphenyldiphosphine in the reaction of diphenylphosphinous chloride with tributylphosphine in the absence of air. The tributylphosphine appeared as its dichloride, suggesting it to function as a reducing agent. Although the mechanism of this process is also unknown, the involvement of the intermediate mentioned previously[4] for the diphosphine dioxide synthesis $[Ar_2P{-}\overset{+}{P}(Cl)Ar_2]$ might receive consideration. This intermediate contains the reducible[8] chlorophosphonium function. It is perhaps significant that P–P bond formation occurs without hydrolysis and oxidation in this reaction. McKechnie, Payne, and Sim[6] have obtained tetraphenyldiphosphine monoxide from the reaction of diphenylphosphinous chloride, water, and triethylamine in the absence of solvent and oxygen. Their reaction is of obvious similarity to that which we had reported earlier,[4] which differs by permitting oxidation to occur.

Regardless of mechanism, the reaction is useful as a simple, one-step synthesis of diphosphine dioxides from phosphinous chlorides. In Table I are provided data on five diphosphine dioxides prepared by this method; yields are in the 50–80% range and may be improvable with further study. The infrared spectra of the compounds confirmed their structure. All contained phosphoryl bands in the 1170–1180-cm^{-1} region. The isomeric anhydride structure (analogous to I) is excluded because of the position of this band and the absence of P–O–P absorption near 965 cm^{-1} (*vide infra*). The full scope of the reaction remains to be estimated. The only failure so far experienced has been with di-n-octylphosphinous chloride; however, dibenzylphosphinous chloride, also lacking a phenyl–phosphorus bond, responded well in the syntheses.

B. Reaction of Ethyl Diphenylphosphinite with Diphenylphosphinic Chloride.—These reactants could presumably give rise to two isomeric products (eq 3).

$$(C_6H_5)_2POC_2H_5 + (C_6H_5)_2POCl \longrightarrow (C_6H_5)_2P(O)P(O)(C_6H_5)_2 \text{ or } \underset{\text{I}}{(C_6H_5)_2P{-}O{-}P(O)(C_6H_5)_2} \quad (3)$$

Anhydrides are known to be formed from various combinations of phosphorus esters and halides,[9] with elimination of alkyl halide, but the reaction has apparently not previously been shown to occur with phosphinites. The diphosphine dioxide would be the result of an Arbuzov-like reaction, but the P–P bond is not known to be formed by this process. We found that an equimolar mixture of the two reactants at room temperature gave a solid product of mp 124–127°, having strong, broad absorption at 965 cm^{-1} in the P–O–P region[10] and at 1240 cm^{-1} in the phosphoryl region. The position of the latter absorption (*cf.* to 1175 cm^{-1} for the diphosphine dioxide) suggests a phosphoryl bearing an electronegative substituent.[10] The product was insoluble in sodium bicarbonate and decolorized potassium permanganate. The product was also obtained by conducting the reaction in ether solution. Analysis showed the compound to have the same composition as tetraphenyldiphosphine dioxide, and it also[3] gave diphenylphosphinic acid and diphenylphosphine oxide on heating in water. We conclude that it is diphenylphosphinic diphenylphosphinous anhydride (I). Only a few anhydrides containing a phosphinous moiety are known; Griffiths and Burg[11] have prepared the symmetrical anhydride of bis-

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[7] S. Frazier, R. Nielsen, and H. Sisler, *Inorg. Chem.*, **3**, 292 (1964).

[8] For some references to other examples, see L. D. Quin and R. E. Montgomery, *J. Org. Chem.*, **28**, 3315 (1963).

[9] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p 338.

[10] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 18.

[11] J. E. Griffiths and A. B. Burg, *J. Am. Chem. Soc.*, **82**, 1507 (1960).

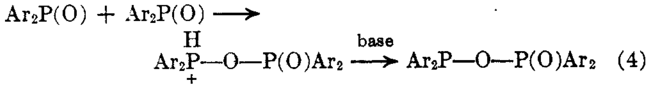
(trifluoromethyl)phosphinous acid, while unsymmetrical anhydrides result from the reaction of diethylphosphinous chloride with some sodium derivatives of dialkyl phosphonates or of alkyl alkylphosphinates.[12] Anhydride I is easily oxidized, and attempts to recrystallize it led to partial conversion to the known[13] diphenylphosphinic anhydride.

C. Reaction of Diphenylphosphine Oxide with Diphenylphosphinic Chloride.—Acylation reactions of secondary phosphine oxides appear not to have been studied previously, and in particular it was unknown whether attack by a phosphinic halide would occur on phosphorus, forming the P–P bond, or on oxygen to form an anhydride. When equimolar amounts of diphenylphosphine oxide, diphenylphosphinic chloride, and diethylaniline were placed in benzene, a white precipitate slowly formed. This was identified as the amine hydrochloride. Solvent was removed from the filtrate and the solid residue, after washing with ether, had mp 124–130°. The solid was insoluble in sodium bicarbonate, decolorized potassium permanganate, and had an infrared spectrum identical with that of the anhydride I. The structure was confirmed as before by hydrolysis. The yield of I was 75% under the best conditions used.

It is thus established that electrophilic attack on a secondary phosphine oxide may occur on oxygen. The resulting change to tricovalent phosphorus is an unusual event, and for secondary phosphine oxides the only other example is that of their conversion to phosphinous chlorides with phosphorus trichloride.[14] The mechanism of these changes is unknown. In the present case, as in the former,[14] the reaction may depend upon a preliminary proton shift to the phosphinous acid form to establish tricovalent phosphorus. Reaction with the phosphinic chloride would then ensue. Another possibility is that the ion, $[\mathrm{Ar_2PO}]^-$, is formed by action of the base, followed by attack of this ion on the chloride. This ion apparently is involved in some

$$\mathrm{Ar_2}\ \mathbf{:O:}\ \text{)r}\ \mathrm{Ar_2\ddot{P}{:}\underset{..}{\ddot{O}}{:}H} \xrightarrow{\text{base}} [\mathrm{Ar_2\ddot{P}{:}\underset{..}{\ddot{O}}{:}}]^-$$

base-catalyzed condensations of secondary phosphine oxides, wherein the phosphorus atom acts as the nucleophilic center.[15] Here the oxygen atom would be the site of nucleophilicity. Similarly, nucleophilicity of the oxygen atom of metal phosphonates may be involved in their formation of anhydrides with phosphinous chlorides.[12] Finally, as in the phosphorus trichloride reaction,[14] nucleophilic attack by the phosphoryl group of the oxide may be considered.



$$\overset{\mathrm{H}}{\mathrm{Ar_2P}}\mathrm{(O)} + \overset{\mathrm{Cl}}{\mathrm{Ar_2P}}\mathrm{(O)} \longrightarrow \underset{+}{\overset{\mathrm{H}}{\mathrm{Ar_2P}}}\mathrm{—O—P(O)Ar_2} \xrightarrow{\text{base}} \mathrm{Ar_2P—O—P(O)Ar_2} \qquad (4)$$

Whatever the mechanism, a duality in the chemical character of secondary phosphine oxides has been revealed, and products derived from them are seen to contain either tri- or tetracovalent phosphorus.

Entirely different behavior was exhibited by dibenzylphosphine oxide. A mixed anhydride analogous to I was anticipated, but the water-insoluble solid which precipitated from the ether solution with the amine salt failed to show P–O–P absorption, and in fact had an infrared spectrum identical in peak positions with tetrabenzyldiphosphine dioxide. Its spectrum differed, however, in having a phosphoryl band of low intensity; its melting point was also low. On recrystallization in the open, the melting point and the intensity of the phosphoryl peak were raised. These observations suggest that the initial precipitate was tetrabenzyldiphosphine monoxide, or a mixture of this and the dioxide. The latter possibility was suggested by proton magnetic resonance studies. Tetrabenzyldiphosphine dioxide showed a sharp singlet for the phenyl protons at 7.23 ppm and a broad apparent doublet (2.98 ppm, $J = 9.5$ cps) for the CH_2 group coupled with P^{31}. The reaction product also showed these features and, in addition, a second phenyl singlet at 7.16 ppm, an unresolved shoulder on the high-field side of the 7.23-ppm peak, and a complex multiplet at 2.75–3.25 ppm. These new absorptions could be attributed to the presence of the diphosphine monoxide. The two different phosphorus atoms could cause the two new phenyl signals, and create two nonequivalent CH_2 groups. Each type of CH_2 could be split by the two different phosphorus atoms, explaining the complexity observed in the 3-ppm region. There was also obtained diphenylphosphinic anhydride from the original filtrate, as well as a small amount of diphenylphosphinic acid. It would appear then that the diphosphine derivative is formed by what amounts to intermolecular dehydration of the secondary phosphine

$$\mathrm{2(C_6H_5CH_2)_2P(O)H + 2(C_6H_5)_2P(O)Cl + 2R_3N \longrightarrow}$$
$$\mathrm{(C_6H_5CH_2)_2P—P(O)(CH_2C_6H_5)_2 + [(C_6H_5)_2P(O)]_2O + 2R_3NHCl} \qquad (5)$$

oxide. The formation of the P–P bond by a thermal dehydration has been observed elsewhere.[16] It will now be of interest to examine other secondary phosphine oxides to determine what course the reaction with phosphinic chlorides takes, and what factors are in control of this course.

D. Dialkylphosphinous Chlorides from Dialkylphosphine Oxides.—Earlier work[14] on the conversion of secondary phosphine oxides to phosphinous chlorides included examples of aromatic derivatives only. It has now been shown that the reaction is applicable also to alkyl derivatives. This reaction has considerable synthetic potential; many secondary phosphine oxides are available from a commercial phosphorus compound by a Grignard reaction,[17] and thus a two-step synthesis of phosphinous halides is possible.

$$\mathrm{RMg + (R'O)_2PHO \longrightarrow R_2P(O)H \xrightarrow{PCl_3} R_2PCl} \qquad (6)$$

The method would appear to compete favorably with existing methods recently summarized.[18] Two new phosphinous chlorides, dibenzyl and di-*n*-octyl, have been prepared in 75.8 and 57% yields from the corresponding oxides.

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(12) B. A. Arbuzov, N. I. Rispoloshenskij, and M. A. Zvereva, *Izv. Akad. Nauk SSSR*, 706 (1958).

(13) N. Kreutzkamp and H. Schindler, *Arch. Pharm.*, **293**, 296 (1960).

(14) R. E. Montgomery and L. D. Quin, *J. Org. Chem.*, **30**, 2393 (1965).

(15) R. C. Miller, J. S. Bradley, and L. A. Hamilton, *J. Am. Chem. Soc.*, **78**, 5299 (1956).

(16) W. A. Henderson, Jr., M. Epstein, and F. S. Seichter, *ibid.*, **85**, 2462 (1963).

(17) R. H. Williams and L. A. Hamilton, *ibid.*, **74**, 5418 (1952).

(18) K. Sasse, "Methoden der Organischen Chemie," Vol. XII, Part I, 4th ed, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1963, p 199.

Experimental Section

General.—Melting points, but not boiling points, are corrected. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra of solids were obtained on KBr pellets; nmr spectra (Varian A-60) were run on deuteriochloroform solutions with tetramethylsilane as internal standard. Literature methods were used for preparing the phosphinous chlorides, (*p*-cyanophenyl)phenyl,[8] (*p*-chlorophenyl)phenyl,[8] and bis(*p*-tolyl),[14] and the phosphine oxides, diphenyl,[8] (*p*-chlorophenyl)phenyl,[8] dibenzyl,[15] and di-*n*-octyl.[17] Commercial diphenylphosphinous chloride was used.

Synthesis of Diphosphine Dioxides.—A typical procedure for the **tetraphenyl derivative** is given in detail; other derivatives were prepared similarly, with minor variations during product isolation. A solution of 11.9 g (0.0539 mole) of diphenylphosphinous chloride in 50 ml of ether was added slowly to a chilled solution of 8.04 g (0.0539 mole) of diethylaniline and 0.60 g (0.033 mole) of water in 60 ml of ether. A white precipitate formed immediately. The mixture was stirred overnight at room temperature, to the atmosphere through a reflux condenser. The precipitate (10.4 g) was collected and washed with water; the soluble amine salt portion weighed 5.76 g. The insoluble material was the crude product. Evaporation of the ether filtrate gave a crystalline solid, which after washing with water provided an additional 3.96 g of crude product. Total yield was 8.60 g (79.4%). After thorough drying, the product was recrystallized from anhydrous acetone–ether or toluene. Water must be carefully excluded in this step to prevent hydrolysis. The use of triethylamine as the base gave a similar yield (77%). The **tetra(*p*-tolyl) derivative** similarly prepared had mp 165–168° (lit.[19] mp 159–163°) and gave the correct analysis before recrystallization. Following recrystallization from ether–tetrahydrofuran, its melting point was raised to 183–185° with no change in its infrared spectrum. This behavior requires further investigation for an explanation. The preparation of the **1,2-di(*p*-chlorophenyl)-1,2-diphenyl derivative** gave the usual precipitate of amine salt and product, but an oil was recovered on stripping solvent from the filtrate. This was dissolved in ether and extracted with 5% hydrochloric acid to remove any residual amine; the ether extract then left a solid on evaporation which proved to be additional product. In the preparation of the **1,2-di(*p*-cyanophenyl)-1,2-diphenyl derivative**, product could only be obtained from the initial precipitate; the filtrate gave a noncrystallizing oil, resisting attempts to remove any additional product therein, and whose infrared spectrum suggested the presence of considerable (*p*-cyanophenyl)phenylphosphine oxide. Attempts to purify the precipitated dioxide by recrystallization gave only oils; the crude product, however, after washing with 5% sodium bicarbonate, water, and then ether, gave the correct analysis. **Tetrabenzyldiphosphine dioxide** was precipitated with the amine salt; none was present in the filtrate. The residue from evaporation of the filtrate was largely dibenzylphosphine oxide, with some dibenzylphosphinic acid. In an attempt to prepare **tetra-*n*-octyldiphosphine dioxide**, the only solid precipitated was the amine salt; from the solution, on chilling in Dry Ice, there was precipitated di-*n*-octylphosphine oxide (50%).

Data for compounds described above appear in Table I.

Reaction of Diphenylphosphine Oxide with Diphenylphosphinous Chloride.—Diphenylphosphine oxide (10.9 g, 0.0539 mole) and triethylamine (5.35 g, 0.0539 mole) in 150 ml of anhydrous ether were treated with 11.9 g (0.0539 mole) of diphenylphosphinous chloride. Air which was dried by passage through a Drierite tube was slowly drawn over the solution, and precipitation of solid commenced immediately. After stirring for 3 hr at room temperature, the solid was filtered and was found to be constituted of 7.2 g of triethylamine hydrochloride and 15.8 g of a mixture of tetraphenyldiphosphine dioxide and diphenylphosphinic diphenylphosphinous anhydride (I) (or diphenylphosphinic anhydride), as indicated by infrared peaks at 1240 and 965 cm^{-1}. An infrared spectrum of a synthetic mixture consisting of 62.5% dioxide and 37.5% anhydride I was qualitatively identical and suggested an approximate composition of the product to be 72% dioxide and 28% anhydride. The yield of diphosphine dioxide (11 g) was 100% based on the diphenylphosphinous chloride charged, but 130% after allowing for consumption of 2.6 g of the chloride in anhydride formation. Thus, some diphenylphosphine oxide must have contributed to the total yield of tetraphenyldiphosphine dioxide. Evaporation of the ether filtrate left a gum which gave no crystalline product on water treatment.

Synthesis of Diphenylphosphinic Diphenylphosphinous Anhydride. A. From Ethyl Diphenylphosphinite.—This ester (2.3 g, 0.01 mole) was treated with 2.36 g (0.01 mole) of diphenylphosphinic chloride. After 12 hr at room temperature, the resulting crystalline mass was washed with ether, and the residue (2.60 g, 65%) was found to melt at 127–130°.

Anal. Calcd for $C_{24}H_{20}O_2P_2$: C 71.64; H, 5.01; P, 15.40. Found: C, 71.47; H, 5.60; P, 15.33.

Recrystallization from toluene–heptane raised the melting point (to 144–147°), but also raised the oxygen content, with no appreciable change in the infrared spectrum. The product appeared to be largely diphenylphosphinic anhydride, mp 142–143°.[13]

Anal. Calcd for $C_{24}H_{20}O_3P_2$: C, 68.90; H, 4.82; P, 14.82. Found: C, 69.37; H, 5.01; P, 15.05.

The unrecrystallized product rapidly decolorized potassium permanganate. In the infrared, it showed a phosphoryl band at 1240 cm^{-1} and broad absorption at 965 cm^{-1}, attributed to the P–O–P group.[20] The product was boiled in water for 20 min and the mixture was extracted with ether. On removal of the ether, a 42% yield of diphenylphosphine oxide, identified by its infrared spectrum, was obtained. Diphenylphosphinic acid was recovered by filtering the water layer.

B. From Diphenylphosphine Oxide.—A solution 4.72 g (0.020 mole) of diphenylphosphinic chloride in 40 ml of benzene was added over a 15-min period to a solution of 4.04 g (0.020 mole) of diphenylphosphine oxide and 2.02 g (0.020 mole) of triethylamine in 60 ml of benzene. The mixture was stirred at 60° for a 2-hr period. The precipitated amine hydrochloride (2.58 g, 94% yield) was removed; on standing, a white solid (1.35 g), identified as diphenylphosphinic acid, separated and was also removed. The filtrate was then stripped of solvent, and the solid residue was washed with ether. The solid (6.0 g, 75% yield) melted at 124–130°; its chemical properties and infrared spectrum were identical with those of diphenylphosphinic diphenylphosphinous anhydride (I).

Reaction of Dibenzylphosphine Oxide with Diphenylphosphinic Chloride.—A solution of 2.36 g (0.010 mole) of diphenylphosphinic chloride in 20 ml of benzene was added to a solution of 2.30 g (0.010 mole) of dibenzylphosphine oxide and 1.01 g (0.010 mole) of triethylamine in 55 ml of benzene. After 2 hr at room temperature, the precipitate was removed. Of the 2.80 g obtained, 1.3 g was water insoluble; this fraction had mp 142–146° and an infrared spectrum showing a phosphoryl peak of low intensity at 1175 cm^{-1}. Recrystallization from benzene–ether raised the melting point to 153–156°, and the infrared spectrum was almost superimposable on that of tetrabenzyldiphosphine dioxide, mp 158–159°. The original benzene filtrate gave on evaporation a solid indicated by its infrared spectrum to be a mixture of diphenylphosphinic acid and its anhydride. This mixture was separated with 5% sodium bicarbonate solution; 0.25 g of the acid and 1.7 g of the anhydride were obtained. The low melting point (125–135°) of the latter was attributed to the presence of some unreacted dibenzylphosphine oxide. Hydrolysis of the anhydride in boiling water gave a 90% yield of diphenylphosphinic acid; a small amount of the oxide was recovered on ether extraction of the hydrolysis mixture.

Dibenzylphosphinous Chloride from Dibenzylphosphine Oxide.—A mixture of 4.5 g of dibenzylphosphine oxide and 27 g of phosphorus trichloride was stirred for 4 hr at room temperature in a nitrogen atmosphere. Liquid was decanted from gummy solids, and then was freed of phosphorus trichloride by distillation. Vacuum distillation of the residue gave 3.70 g (75.8% yield) of dibenzylphosphinous chloride at 131–135° (0.25–0.35 mm). This compound is very readily oxidized and hydrolyzed, and its analysis was not attempted. It was identified by hydrolysis to dibenzylphosphine oxide.

Di-*n*-octylphosphinous Chloride from Di-*n*-octylphosphine Oxide.—A mixture of 7.0 g of the oxide and 35 g of phosphorus trichloride after a 3-hr period was worked up as above, giving 3.5 g (57% yield) of di-*n*-octylphosphinous chloride, bp 132–135° (0.25–0.35 mm). It was identified by hydrolysis to di-*n*-octylphosphine oxide.

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(19) K. Okon, J. Sobczynski, J. Sowinski, and K. Niewielski, *Biul. Wojskowej Akad. Tech.*, **13**, 109 (1964); *Chem. Abstr.*, **62**, 4050*f* (1965).

(20) These values are within experimental error of those reported for diphenylphosphinic anhydride (1236 and 962 cm^{-1}, respectively): K. Moedritzer, *J. Am. Chem. Soc.*, **83**, 4381 (1961).