THE PREPARATION AND PROPERTIES OF TERTIARY AND SECONDARY PHOSPHINE OXIDES

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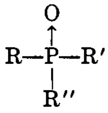
CONTENTS

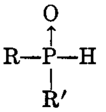
I. INTRODUCTION

The most recent review on tertiary phosphine oxides constituted the sixth chapter of Kosolapoff's book published in 1950 (69). Much of the work reported at that time was from very old literature in which procedures were sometimes too briefly described. Although the field has been neglected somewhat, as compared to other areas of organophosphorus chemistry, progress has been made to improve classical methods for the synthesis of a variety of tertiary phosphine oxides. This is especially true in the past decade. The remarkable stability of these compounds should itself be a stimulus for future research. Emphasis is placed on developments since 1950, although references to earlier work are included in certain sections for the sake of completeness. This discussion will be limited to those tertiary phosphine oxides which possess a phosphorus atom bonded to three carbon atoms and to an oxygen atom. The lines joining phosphorus with R, R′, and R″, respectively, represent carbon–phosphorus linkages.



$$\mathrm{R{-}\underset{\underset{R''}{|}}{\overset{\overset{O}{\uparrow}}{P}}{-}R'}$$

Secondary phosphine oxides have been understood only since 1952, when the first dialkylphosphine oxides were synthesized (106). Although this class of compounds is relatively new, they can be prepared by several methods, most of which afford fair yields. Very few reactions of secondary phosphine oxides are known, however. The general structure of these oxides is illustrated by the formula below. Only those compounds in which R and R′ contain a carbon atom bonded to the central phosphorus atom are discussed.



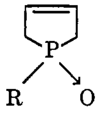
$$\mathrm{R{-}\underset{\underset{R'}{|}}{\overset{\overset{O}{\uparrow}}{P}}{-}H}$$

It is the purpose of this review to examine and to evaluate the various methods used to prepare tertiary and secondary phosphine oxides. Spectral properties and some reactions of the oxides are summarized also. Tables are included which contain physical data on both types of compounds. Oxides which were not characterized in the original references have been omitted. *Chemical Abstracts* is covered through September 10, 1959.

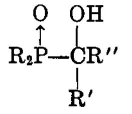
NOMENCLATURE

The nomenclature of the tertiary phosphine oxides used in this review was that established by the Nomenclature Committee of the American Chemical Society and published in *Chemical and Engineering News* on October 27, 1952 (2). It should be noted that secondary phosphine oxides are listed in *Chemical Abstracts* under "Phosphinous acids" as well as under "Phosphine oxides." Experimental evidence now available indicates that the name which better represents the structure of this class of compounds is secondary phosphine oxide and not phosphinous acid.

Certain tertiary phosphine oxides with rather unique structures have been reported. For example, the cyclic compound I is listed as a 1-substituted phospha-3-cyclopentene *P*-oxide (76); the authors have elected to use this nomenclature. A more recent report has labeled such oxides as substituted phospholine 1-oxides (56). Disubstituted phosphinyl alcohols are the series of compounds described by the general formula II (86). A specific example would be α-(dibenzylphosphinyl)-benzyl alcohol (III). The addition of secondary phosphine oxides to α,β-unsaturated nitriles and carbonyl compounds resulted in the preparation of the tertiary phosphine oxides illustrated by formula IV (84). As an example compound V is listed as 3-dibenzylphosphinylpropionic acid.

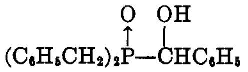


I



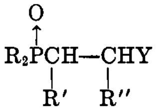
$$\mathrm{R_2\overset{\overset{O}{\uparrow}}{P}{-}\underset{\underset{R'}{|}}{\overset{\overset{OH}{|}}{C}}R''}$$

II



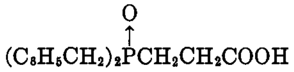
$$\mathrm{(C_6H_5CH_2)_2\overset{\overset{O}{\uparrow}}{P}{-}\overset{\overset{OH}{|}}{C}HC_6H_5}$$

III



$$\mathrm{R_2\overset{\overset{O}{\uparrow}}{P}\underset{\underset{R'}{|}}{C}H{-}\underset{\underset{R''}{|}}{C}HY}$$

IV



$$\mathrm{(C_6H_5CH_2)_2\overset{\overset{O}{\uparrow}}{P}CH_2CH_2COOH}$$

V

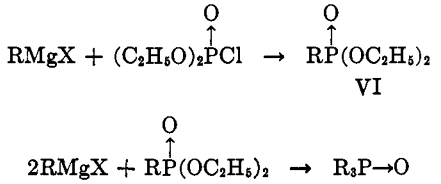
II. Recent Developments in the Preparation of Phosphine Oxides

A. TERTIARY PHOSPHINE OXIDES

1. *The use of Grignard reagents*

The preparation of tertiary phosphine oxides via the reaction of Grignard reagents with halides and/or esters of phosphorus acids was described in a previous review (69). Prior to 1950, however, very little was known concerning the effects of various concentrations of reagents, the influence of the leaving group in the ester, and the most ideal solvent system for maximum yield of product. Since that time several investigations have been carried out on this type of synthesis with more emphasis placed on such factors as those mentioned.

The use of dialkyl chlorophosphates as starting materials in the synthesis of phosphonic acids has been reviewed recently (33). Actually the former class of compounds can serve as reagents in the preparation of tertiary phosphine oxides as reported by Burger and Dawson (12). The general reaction is given in the equation in which diethyl chlorophosphate is used. With



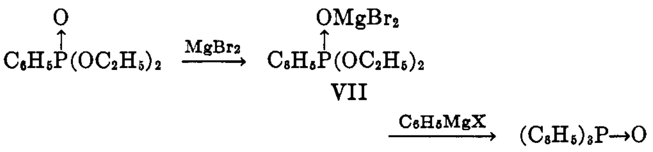
$$\mathrm{RMgX + (C_2H_5O)_2\overset{\overset{O}{\uparrow}}{P}Cl \rightarrow \underset{VI}{R\overset{\overset{O}{\uparrow}}{P}(OC_2H_5)_2}}$$

$$\mathrm{2RMgX + R\overset{\overset{O}{\uparrow}}{P}(OC_2H_5)_2 \rightarrow R_3P{\rightarrow}O}$$

ortho-substituted aryl Grignard reagents (moles of RMgX to moles of $(C_2H_5O)_2(Cl)P{\rightarrow}O = 1{:}1$) it was possible to obtain good yields of the substituted phosphonate VI. It was suggested that a steric effect created by the ortho group retarded further reaction of compound VI with the Grignard reagent under the conditions specified. Tertiary phosphine oxides were prepared in good yields by the use of Grignard reagents which were not substituted in the ortho position. However, a reversal of addition, that is, the addition of the Grignard reagent to diethyl chlorophosphate, was found to give chiefly phosphonates also. Thus it was suggested that in the presence of an excess of Grignard reagent, the tertiary phosphine oxide might predominate in the products. Excellent yields of several symmetrical phosphine oxides were obtained by employing an excess of Grignard reagent. Apparently the displacement of the ethoxy group is not a difficult task. Kosolapoff cited one or two early examples in which an ethoxy or phenoxy function was replaced in a similar manner (69). On the basis of Kosolapoff's report that diethyl phenyl phosphonate did not react with the phenyl Grignard reagent to give a phosphine oxide (67), Dawson and Burger ruled out the possibility of a phosphonate

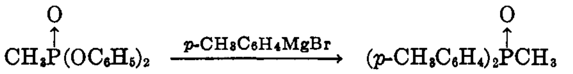
$$[(R'O)_2(R)P\rightarrow O]$$

as an intermediate (27) in their reaction. They were able to show, however, that if magnesium bromide was mixed with diethyl phenylphosphonate and the resulting mixture was added to the phenyl Grignard reagent, triphenylphosphine oxide could be isolated in a yield of 55 per cent. An activated complex (VII) was postulated in which the phosphoryl oxygen atom was coördinated with the magnesium bromide. Apparently, through coordination of the oxygen atom, the phosphorus atom of the complex (VII) was made more sensitive to nucleophilic attack.



$$C_6H_5\overset{\overset{O}{\uparrow}}{P}(OC_2H_5)_2 \xrightarrow{MgBr_2} \underset{VII}{C_6H_5\overset{\overset{OMgBr_2}{\uparrow}}{P}(OC_2H_5)_2} \xrightarrow{C_6H_5MgX} (C_6H_5)_3P\rightarrow O$$

It has since been demonstrated that diphenyl phenylphosphonate, when treated with an excess of the Grignard reagent, can serve as an intermediate in the preparation of tertiary phosphine oxides (8). Forcing conditions (ether–benzene solvent system) were necessary to afford the highest yields. The method is similar to that used to convert diphenyl methylphosphonate to di(p-tolyl)methylphosphine oxide in 60 per cent of the theoretical quantity (87). In several investigations (38, 67, 75) concerned with this type of displacement reaction involving esters of phosphorus acids, it seems likely that a low concentration of Grignard reagent was one factor influencing their failure to yield tertiary phosphine oxides. Incomplete reaction of a phosphonate could lead to formation of a phosphinate or, after hydrolysis, the corresponding phosphinic acid.



$$CH_3\overset{\overset{O}{\uparrow}}{P}(OC_6H_5)_2 \xrightarrow{p\text{-}CH_3C_6H_4MgBr} (p\text{-}CH_3C_6H_4)_2\overset{\overset{O}{\uparrow}}{P}CH_3$$

By examination of existing data on the synthesis of tertiary phosphine oxides from esters of phosphorus acids, it is possible to arrive at a few conclusions concerning the nature of the reaction in question. That the replacement of alkoxy (or aryloxy) groups from phosphorus esters occurs in a stepwise manner has been generally accepted. The classes of esters involved are: phosphates, $(RO)_3P\rightarrow O$; phosphonates, $(RO)_2(R')P\rightarrow O$; phosphinates, $(RO)(R')_2P\rightarrow O$; phosphites, $(RO)_3P$. With regard to the esters possessing a phosphoryl function, the electron density on the phosphorus atom undoubtedly varies even when the phosphoryl oxygen atom is coördinated with a Grignard reagent. It would be difficult to predict reactivity in a series of phosphates, phosphonates, and phosphinates which were similarly substituted. The p electrons on the oxygen atoms of the RO groups may alleviate some of the electronic deficit on the phosphorus atom through resonance. This is possible since phosphorus has $3d$ orbitals vacant which can permit an expansion of its valence shell to ten electrons. If R′ possessed excessive electron-donating ability, such as might be the case with

$$R' = p\text{-}CH_3OC_6H_4\text{—}$$

the effect of coördination might be somewhat nullified.

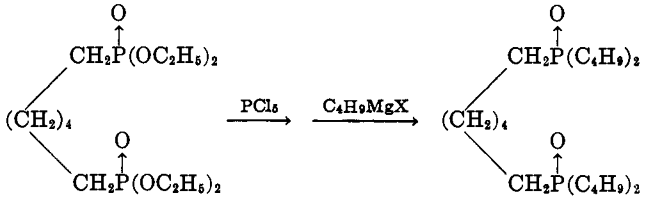
Another point which has apparently gone unnoticed is the nature of the leaving group. Triphenylphosphine oxide was formed in low yields when triphenyl phosphate was allowed to react with the phenyl Grignard reagent (39). Some years later the reaction of triethyl phosphate with the phenyl Grignard reagent resulted in the production of diethyl phenylphosphonate and diphenylphosphinic acid. Formation of these compounds probably is the result of incomplete reaction of triethyl phosphate with the Grignard reagent. The fact that a phenoxy group was displaced more readily than an ethoxy function seems important. As mentioned previously, diphenyl phenylphosphonate was receptive to attack by Grignard reagents, and yields greater than 50 per cent of unsymmetrical tertiary phosphine oxides of the type $RR'(C_6H_5)P\rightarrow O$ ($R = R' =$ alkyl) were realized (8). It had been shown (67) that diethyl phenylphosphonate, $(C_2H_5O)_2(C_6H_5)P\rightarrow O$, did not yield a tertiary phosphine oxide when treated with the phenyl Grignard reagent, even with prolonged heating at 85–95°C. Since an excess of Grignard reagent was not used in this reaction, it is probably unfair to compare the reactions. Another example in which a phenoxy group was displaced occurred in the preparation of di(p-tolyl)-methylphosphine oxide from diphenyl methylphosphonate; again forcing conditions were needed (87). Thus the stability of the leaving group may be an important factor in promoting a favorable equilibrium. In the examples discussed the resonance-stabilized phenoxide ion would be more stable than the ethoxide species.

Phosphites $[(RO)_3P]$ do not possess a semipolar phosphorus–oxygen bond; thus this class of esters would be expected to yield phosphine derivatives. When trimethyl phosphite was treated with the phenyl Grignard reagent, methyldiphenylphosphine oxide was produced in 42 per cent yield (38). The formation of this phosphine oxide was explained as resulting from rearrangement *in situ* of an intermediate, namely a phosphinate $[R_2POR']$. This classical Michaelis–Arbuzov isomerization has been known to occur with similar esters in the absence of any catalyst or other reagent (see reference 69 for a discussion and references). A slight excess of the phenyl Grignard reagent with triethyl phosphite resulted in a 10 per cent yield of triphenylphosphine oxide (38). This reaction has been examined more closely by Maguire and Shaw (75). By use of equal molar ratios of triethyl phosphite and the phenyl Grignard reagent, triphenylphosphine oxide (14 per cent) was obtained along with phenylphosphonous acid (15.3 per cent), diphenylphosphinic acid (7.2 per cent), and biphenyl (6.7 per cent). A 2:1 molar ratio of phosphite to Grignard agent resulted in the formation of triphenylphosphine oxide (10 per cent), diphenylphosphinic acid (20 per cent), phenylphosphonous acid (5.3 per cent), nearly one mole of triethyl phosphite, and a neutral compound. As with the other esters, the stepwise displacement of the RO groups is probable in reactions of phosphites with Grignard reagents. The formation of phenylphosphonous acid and diphenylphosphinic acid could result via hydrolysis of their corresponding ethyl esters. At present the other esters of phosphorus acids are preferred for the direct preparation of tertiary phosphine oxides, since the reactions involved do not appear to be as prone to side occurrences. Tertiary phosphines produced from the condensation of phosphites with Grignard reagents require a second step, namely an oxidation, to give tertiary phosphine oxides.

Several factors have presented themselves with regard to the preparation of tertiary phosphine oxides from esters of phosphorus acids. The nature of the leaving group, the electronic character of the phosphorus atom, and the concentration of the Grignard reagent appear to be important. The reactivity of the Grignard reagent is probably influential also, but no such study has been published. One might anticipate that use of a more aggressive reagent would tend to counteract the inertness of the phosphorus atom to nucleophilic attack. That this is indicated will be shown in the discussion concerned with organolithium compounds as reagents for the preparation of tertiary phosphine oxides.

The use of phosphorus oxychloride, phosphonyl halides, and phosphinyl halides as starting materials for the synthesis of tertiary phosphine oxides was known before the turn of the century (69). Symmetrical tertiary phosphine oxides ($RR'R''P\rightarrow O$: $R = R' = R''$) can be prepared easily via the reaction of phosphorus oxychloride with an excess of the particular Grignard reagent (34, 35, 65, 67, 69, 104). In 1950 an excellent article appeared which was devoted to the use of phosphinyl chlorides as precursers for the preparation of unsymmetrical tertiary phosphine oxides of the type $RR'R''P\rightarrow O$ ($R = R' =$ aryl $\neq R'' =$ alkyl) (89). A thirty-mole excess of the Grignard reagent was employed, and the yields of tertiary phosphine oxides were greater than 65 per cent, the one exception being diphenylisopropylphosphine oxide (44.6 per cent yield). A control experiment was performed whereby diphenylphosphinic acid, $(C_6H_5)_2(OH)P\rightarrow O$, was treated with ethyl Grignard reagent. The acid was recovered unchanged, as expected.

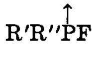
A patent describes, in a brief way, the preparation of several unsymmetrical tertiary phosphine oxides using as starting materials phosphonyl halides and phosphinyl halides (88). For example, compound VIII was obtained in a yield of 23 per cent. This di-tertiary-phosphine oxide (VIII) was prepared by reaction of the corresponding tetrachloride derivative with the *n*-butyl Grignard reagent, as shown in the equation. Conditions of the final step in the synthesis were not well defined. Several tertiary phosphine oxides of unusual structure were synthesized, but no physical data were included for them.



VIII

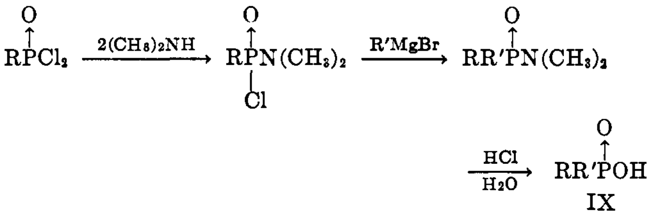
There have been other reports of work with phosphorus acid halides, but the quantities of starting materials as well as reaction conditions were poorly defined or absent entirely (9, 53). As mentioned previously, in the presence of a large excess of Grignard reagent, good yields of unsymmetrical tertiary phosphine oxides can be obtained from the phosphinyl chlorides (89). The reaction of phosphonyl and phosphinyl halides with Grignard reagents has been assumed to be relatively straightforward, although investigations in this area have not been extensive. Di(*p*-tolyl)phenylphosphine oxide was prepared in 82 per cent yield from the condensation of phenyldichlorophosphine oxide with the *p*-tolyl Grignard reagent (87). However, an attempt to prepare diallylphenylphosphine oxide in a similar reaction failed (8).

The organofluorine compounds represented by the formulas below might be very reactive to nucleophilic attack by Grignard or lithium reagents, owing to the powerful inductive effect of fluorine. Methyldifluorophosphine oxide, $CH_3F_2P\rightarrow O$, was recently synthesized (28). The compound was treated with several Grignard reagents, and phosphinic acids were the result. With respect to production of phosphine oxides, however, the reactions were run under poor conditions, since equivalent amounts of methyldifluorophosphine oxide and the Grignard reagent were used; the latter was never in excess.


$R'R''\overset{\overset{O}{\uparrow}}{P}F$

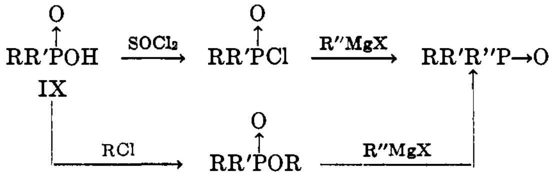

$R\overset{\overset{O}{\uparrow}}{P}F_2$

The research of Crofts and Fox may have opened a new route to tertiary phosphine oxides of the formula RR′R″P→O, where R ≠ R′ ≠ R″ (23).



$$\mathrm{R\overset{O}{\overset{\uparrow}{P}}Cl_2} \xrightarrow{2(\mathrm{CH_3})_2\mathrm{NH}} \mathrm{R\overset{O}{\overset{\uparrow}{\underset{Cl}{P}}}N(CH_3)_2} \xrightarrow{\mathrm{R'MgBr}} \mathrm{RR'\overset{O}{\overset{\uparrow}{P}}N(CH_3)_2} \xrightarrow[\mathrm{H_2O}]{\mathrm{HCl}} \underset{\mathrm{IX}}{\mathrm{RR'\overset{O}{\overset{\uparrow}{P}}OH}}$$

The second mole of dimethylamine reacts with the hydrogen chloride produced *in situ*. It is apparent from previous discussion that the phosphinic acid IX could be converted to a phosphinyl halide which in turn could be treated with a different Grignard reagent or lithium compound. As shown in the alternative scheme, an ester of the phosphinic acid could be treated with an organometallic reagent to give the unsymmetrical tertiary phosphine oxide.



$$\begin{tikzcd}
\underset{\mathrm{IX}}{\mathrm{RR'\overset{O}{\overset{\uparrow}{P}}OH}} \arrow[r, "\mathrm{SOCl_2}"] \arrow[dr, "\mathrm{RCl}"'] & \mathrm{RR'\overset{O}{\overset{\uparrow}{P}}Cl} \arrow[r, "\mathrm{R''MgX}"] & \mathrm{RR'R''P\to O} \\
 & \mathrm{RR'\overset{O}{\overset{\uparrow}{P}}OR} \arrow[ur, "\mathrm{R''MgX}"'] &
\end{tikzcd}$$

2. The use of lithium reagents

No thorough study has been reported on the application of lithium reagents in the preparation of tertiary phosphine oxides. The first recorded investigation in this area appears to be that of Mikhailov and Kucherova (81, 82). They reported the synthesis of symmetrical tertiary phosphine oxides (RR′R″P→O: R = R′ = R″) by the action of various lithium reagents on phosphorus oxychloride; the molar ratio was 3:1, respectively. Since the reaction was vigorous, it was carried out at ice-bath temperatures; the yields of tertiary phosphine oxides ranged from 38 to 65 per cent. An alteration in the proportions of starting materials failed to produce any other products except the tertiary phosphine oxides. However, the abstract lacks sufficient experimental detail concerning changes in the concentrations of starting materials.

When the lithium reagent prepared from *p*-bromodimethylaniline was allowed to react with a nearly equal molar quantity of phosphorus oxychloride, tris(*p*-dimethylaminophenyl)phosphine oxide resulted in 50.4 per cent yield (97). A by-product, bis(dimethylaminophenyl)phosphinic acid, was also isolated (11.7 per cent yield). The reaction was carried out in ether with cooling and without a large excess of either reagent; this is an advantage over the Grignard method, since it usually requires more strenuous conditions to give good returns.

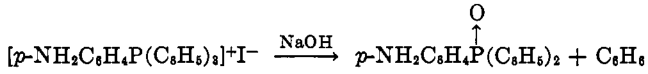
Certain esters of phosphorus acids were treated with lithium reagents, and the results were quite encouraging, as recorded yields of tertiary phosphine oxides were 80 per cent or better (105). When treated with phenyllithium, trialkyl phosphates were reported to give triphenylphosphine oxide in high yield. In the presence of three moles of phenyllithium, one mole of diethyl chlorophosphate afforded triphenylphosphine oxide in 80 per cent of the theoretical amount. The yield was better than when the corresponding Grignard reagent was employed (12, 27). That triethyl phosphite was easily converted to triphenylphosphine (105) seems to indicate that the powerful lithium compounds may be the reagents of choice to minimize the formation of side products which often result from incomplete reaction of esters of phosphorus acids with Grignard reagents. Trialkyl phosphites are rather sluggish in reacting with Grignard reagents, and frequently a series of compounds (all in low yield) are produced (39, 75).

Although the available data are meager in quantity, it suggests that organolithium compounds are superior to Grignard reagents in the synthesis of tertiary phosphine oxides from esters of phosphorus acids. With the large choice of lithium reagents now available, preparation of a wide variety of phosphine oxides should be possible through reaction with the phosphates, phosphonates, and phosphinate esters as well as with the substituted phosphorus oxychloride derivatives.

3. Decomposition of quaternary phosphonium compounds in basic solution

The decomposition of quaternary phosphonium compounds was described by Kosolapoff in 1950 (69), but work which he reported had been done more than fourteen years earlier. An examination of the early literature revealed that phosphonium salts had never been fully investigated as possible starting materials for the preparation of tertiary phosphine oxides. Several references to some of the pioneering research are included here, although they can be found in Kosolapoff's review (17, 18, 30, 31, 48–50, 74, 78–80). Very often quantities of reagents as well as yields of products were not included in the reports. There have been a series of publications since 1950 which suggest that this reaction merits the classification as an excellent preparative method for tertiary phosphine oxides. The extensive work of Horner and coworkers in a series of papers (52–54) was concerned chiefly with the synthesis of triarylphosphine oxides. When the quaternary aryl phosphonium halide was treated with 20 per cent aqueous sodium hydroxide, the most electronegative aryl group was lost. For example, *p*-chlorophenyltriphenylphosphonium iodide decomposed to give triphenylphosphine oxide (93 per cent yield) and chlorobenzene. In contrast, benzene was eliminated when *p*-aminophenyltriphenylphosphonium iodide was treated with base; the yield of *p*-aminophenyldiphenylphosphine oxide was 95 per cent. Most of the more than twenty tertiary phosphine oxides reported were obtained in yields greater than 85 per cent. The reaction appears general for quaternary aryl phosphonium compounds, and since the procedure

$$[p\text{-}ClC_6H_4P(C_6H_5)_3]^+I^- \xrightarrow{NaOH} (C_6H_5)_3P{\rightarrow}O + C_6H_5Cl$$

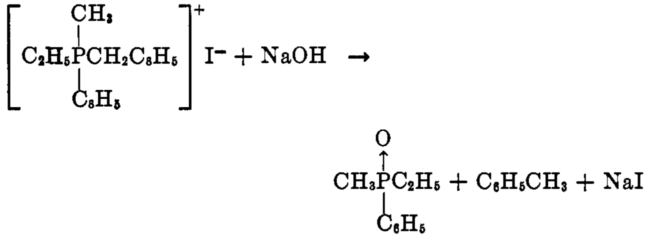


$$[p\text{-}NH_2C_6H_4P(C_6H_5)_3]^+I^- \xrightarrow{NaOH} p\text{-}NH_2C_6H_4\overset{\overset{O}{\uparrow}}{P}(C_6H_5)_2 + C_6H_6$$

is not elaborate, the method is excellent for the preparation of triarylphosphine oxides of the type RR′R″P→O, where R = R′ ≠ R″.

In 1952 a study was made of the decomposition of several alkyltriarylphosphonium halides in the presence of 40 per cent aqueous potassium hydroxide (87). The formation of alkyldiarylphosphine oxides was in agreement with earlier results by Fenton and Ingold, who determined the preferential loss of groups as benzyl > phenyl > phenethyl > ethyl > higher alkyls (31). In the few cases examined by the more recent investigators, the yields of tertiary phosphine oxides were in excess of 80 per cent (87). By previous work the hydroxide salt had been shown to be the intermediate which decomposed (17, 18, 31, 49, 69, 74, 78–80, 98). Thus the reaction appears analogous to pyrolyses involving the hydroxide salts of quaternary ammonium compounds.

Recently an interesting discovery was made in connection with the decomposition of certain quaternary phosphonium salts (72, 73, 110). When optically pure levorotatory methylethylphenylbenzylphosphonium iodide (72) was treated with aqueous methanolic sodium hydroxide at 100°C. for 10 hr., toluene and dextrorotatory methylethylphenylphosphine oxide were produced. The quantity of the tertiary phosphine oxide (X) isolated was 89 per cent of theory (73). The dextrorotatory phosphonium salt decomposed to give the levorotatory tertiary phosphine oxide. Although the reactions appear to be stereospecific, it has not, as yet, been possible to determine whether the mechanism involves retention or inversion at the phosphorus atom. A kinetic study of the decomposition in a series of p-Z-benzyltribenzylphosphonium halides (where Z = NO_2, Cl, H, CH_3, or CH_3O) showed the reaction to be first order in phosphonium ion and second order in hydroxide ion (110). The ease of elimination of groups parallels the anionic stability, a result which is in agreement with previous work (54).



$$\left[\begin{array}{c} CH_3 \\ | \\ C_2H_5PCH_2C_6H_5 \\ | \\ C_6H_5 \end{array}\right]^+ I^- + NaOH \rightarrow CH_3\overset{\overset{O}{\uparrow}}{P}C_2H_5 + C_6H_5CH_3 + NaI$$

$$\text{with } C_6H_5 \text{ on P of the product}$$

X

4. *Miscellaneous*

(a) Oxidation of phosphines

In contrast to the preparative methods in which tertiary phosphine oxides can be obtained directly from oxygen-containing intermediates, the tertiary phosphines required here must be synthesized and then allowed to undergo oxidation. Aromatic phosphines are often resistant to oxidation (34, 69). This is not too surprising, since the pair of unshared valence electrons on phosphorus in phosphines can interact with bonded aryl groups as evidenced by ultraviolet absorption measurements (61, 62). Selection of a suitable oxidizing agent can be troublesome, as readily oxidizable alkyl groups on the phosphorus atom and on the side chains of aromatic substituents may be involved in the reaction. The references to oxidation of phosphines with alkyl or aryl peroxides (29, 40, 51, 55), hydrogen peroxide (44, 59, 71, 95, 97, 101), nitrogen tetroxide (1), nitric acid (91, 100), and amine oxides (57) denote work done in this area since 1950. It should be mentioned also that phosphines are frequently converted to the oxides upon standing in air or in the presence of oxygen (5, 69).

Quite frequently, tertiary phosphines are used as specific reducing reagents, but since the conversion of the phosphines to tertiary phosphine oxides is of secondary interest, the yields are reported only rarely. These articles are not included in the bibliography, but many are cited in the references given in this section.

(b) Rearrangements

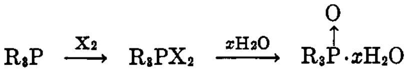
The mechanism of the isomerization of phosphinites to phosphine oxides is not completely understood. The general reaction is given in the equation and may be classified as an example of the Arbuzov rearrangement.

$$RR'POR'' + R'''X \rightarrow RR'R'''P{\rightarrow}O + R''X$$

Such esters can undergo rearrangement in the presence of a catalyst, although not infrequently the isomerization is self-catalyzed (69). Consequently, this side reaction decreases the value of the method for the preparation of tertiary phosphine oxides. Although recent reports (3, 4, 63, 64, 101) have verified earlier work (69), extensive research in the area is too limited to be of value in the synthesis of tertiary phosphine oxides.

(c) Hydrolysis of tertiary phosphine dihalides

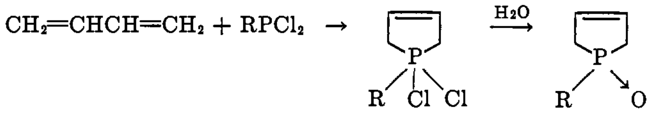
The reaction shown in the equation was reported to occur readily (69), but it has several disadvantages. The



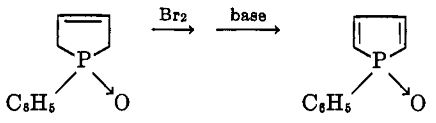
$$R_3P \xrightarrow{X_2} R_3PX_2 \xrightarrow{xH_2O} R_3\overset{\overset{O}{\uparrow}}{P}\cdot xH_2O$$

dihalides are known to be unstable (69) and are generally not purified. It is apparent that phosphines which contain functional groups capable of reacting with halogens could lead to undesirable mixtures of tertiary phosphine oxides. Most tertiary phosphine oxides form hydrates which often require heating near 100°C. in a vacuum over powerful drying agents before decomposition occurs to give the pure oxide.

Some research has been recorded on tertiary phosphine dihalides since 1950 (56, 76, 77, 92, 97, 109). A particularly interesting group of cyclic phosphine oxides was recently prepared via a tertiary phosphine dihalide intermediate (56, 76, 77). Although synthesis of the cyclic dihalide differs from the classical method discussed previously, the addition of trivalent phosphorus halides, such as phosphorus trichloride, to unsaturated compounds has been known for some time (20, 69). The cyclic phosphine oxides (XI) are stable up to 300°C. and have insecticidal properties (76). Bromination of the phenyl derivative (XII) gave a dibromide which when treated with organic bases gave a diene; the latter dimerized on standing (56). At present no properties of the dimer have been recorded in the literature.

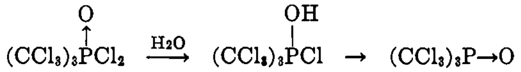


XI



XII

Partial hydrolysis of tris(trichloromethyl)dichlorophosphine has been reported to give a compound (XIII) of unique structure (109). When treated with aniline, compound XIII decomposed to yield tris(trichloromethyl)phosphine oxide.



$$(CCl_3)_3\overset{\overset{O}{\uparrow}}{P}Cl_2 \xrightarrow{H_2O} (CCl_3)_3\overset{\overset{OH}{|}}{P}Cl \rightarrow (CCl_3)_3P\rightarrow O$$

XIII

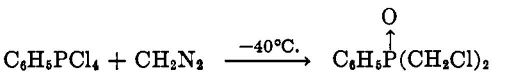
Tris(trifluoromethyl)phosphine oxide (in 70 per cent yield) was obtained when tris(trifluoromethyl)dichlorophosphine was treated with anhydrous oxalic acid.

$$(CF_3)_3PCl_2 + H_2C_2O_4 \rightarrow (CF_3)_3P\rightarrow O + CO + CO_2 + 2HCl$$

Hydrolysis with water gave bis(trifluoromethyl)phosphinic acid and fluoroform (92).

(d) Miscellaneous

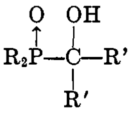
The use of diazoalkanes to prepare organophosphorus compounds, including phosphine oxides, was described briefly in a review (98). A novel phosphine oxide, bis(chloromethyl)phenylphosphine oxide, was synthesized in 34 per cent yield by this procedure (108). It would be premature to make an evaluation of the method for the preparation of phosphine oxides, since



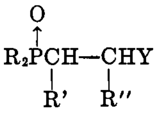
$$C_6H_5PCl_4 + CH_2N_2 \xrightarrow{-40^\circ C.} C_6H_5\overset{\overset{O}{\uparrow}}{P}(CH_2Cl)_2$$

only a few experiments have been recorded on the subject.

A series of rather unusual tertiary phosphine oxides have been realized by the addition of secondary phosphine oxides [$R_2(H)P\rightarrow O$] to aldehydes, ketones, and α,β-unsaturated amides, esters, ketones, and nitriles (84, 86, 95). General formulas for the products are given below. The preparative reaction will be discussed in the section concerned with the chemistry of secondary phosphine oxides. Its value in the synthesis of tertiary phosphine oxides is limited somewhat, since relatively few secondary phosphine oxides are known. It should also be noted that compounds of the general structures II and IV were reported many years ago (20). The preparations involved the addition of diphenylchlorophosphine to functions similar to those described above. The products were not well characterized, however.



II



IV

B. SECONDARY PHOSPHINE OXIDES

In the previous review (69) reference was made to the preparation of a few phosphinous acids, none of which were well defined. There is experimental evidence to indicate that phosphinous acids are better described as secondary phosphine oxides, which are represented by the general formula below.

$$RR'\overset{\overset{O}{\uparrow}}{P}H$$

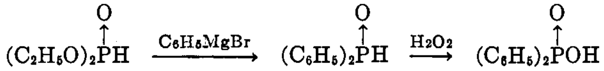
1. *Synthesis by use of organometallic reagents*

The first systematic study concerned with the synthesis of secondary phosphine oxides was described by Williams and Hamilton (106), although the previous year Kosolapoff and Watson reported that di(n-propyl)phosphine oxide and di(n-butyl)phosphine oxide had been obtained as crude intermediates (70). The reaction involved treatment of the appropriate Grignard reagent with a solution of di(n-butyl) phosphonate,

$$(C_4H_9O)_2(H)P\rightarrow O$$

in ether (106). It was necessary to reflux the mixture after the addition was complete. When the quantity of phosphonate was reduced by one-half (with the same total concentration of Grignard reagent present), a higher yield of secondary phosphine oxide was obtained (107). The reaction is comparable to the preparation of tertiary phosphine oxides from esters of phosphorus acids. By the use of large quantities of starting materials, dibenzylphosphine oxide was realized in 70 per cent yield. Since the di(*n*-butyl) phosphonate was added to the benzyl Grignard reagent, the latter was always present in excess (84). Members of the alkyl series from C_1 to C_4 were reported early to be unstable. Distillation of the crude liquid obtained from the Grignard reaction gave the corresponding phosphinic acid (107). However, di(*n*-butyl)phosphine oxide has been prepared recently by the oxidation of di(*n*-butyl)phosphine (96).

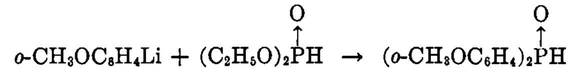
Diphenylphosphine oxide was obtained in 48 per cent yield from the reaction of diethyl phosphonate with the phenyl Grignard reagent (approximately 1.4 mole excess) (58). As proof of structure, the secondary phosphine oxide was oxidized to the corresponding phosphinic acid.



$$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}H \xrightarrow{C_6H_5MgBr} (C_6H_5)_2\overset{O}{\overset{\uparrow}{P}}H \xrightarrow{H_2O_2} (C_6H_5)_2\overset{O}{\overset{\uparrow}{P}}OH$$

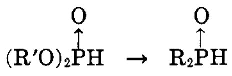
When the di-Grignard reagent of pentamethylene dibromide was allowed to react with di(*n*-butyl) phosphonate, polymeric material resulted. A trisubstituted product was reported also but was not characterized (68).

Lithium compounds have been used only sparingly as reagents in the preparation of secondary phosphine oxides. In a lone article the isolation of bis(*o*-methoxyphenyl)phosphine oxide was described (yield 59 per cent) (105). Diphenylphosphine oxide and bis(*p*-methoxyphenyl)phosphine oxide prepared in a similar way were oxidized in crude form to the corresponding phosphinic acids in good yields. The more aggressive lithium reagents might be expected to be superior to Grignard reagents, although experimental data are lacking with which to make a comparison.



$$o\text{-}CH_3OC_6H_4Li + (C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}H \rightarrow (o\text{-}CH_3OC_6H_4)_2\overset{O}{\overset{\uparrow}{P}}H$$

Several factors are probably involved in the conversion of disubstituted phosphonates to secondary phosphine oxides by the use of lithium or Grignard reagents. The electronic deficiency on the phosphorus atom and the nature of the leaving group may be important. Coördination of the phosphoryl oxygen atom would be expected to increase the sensitivity of the phosphorus atom (in the phosphonate) to nucleophilic attack by an organometallic reagent. No study has been made to determine if different leaving groups in the disubstituted phosphonates (R′ is varied) influence the reaction. It has been shown that the phenyl ester of substituted phosphonic acids [$(C_6H_5O)_2(R)P\rightarrow O$] can serve as starting materials in the synthesis of tertiary phosphine oxides (8, 87). The use of diphenyl phosphonate, which was prepared recently (103), might offer an advantage in the preparation of secondary phosphine oxides, since the phenoxide ion is a resonance-stabilized leaving group.



$$(R'O)_2\overset{O}{\overset{\uparrow}{P}}H \rightarrow R_2\overset{O}{\overset{\uparrow}{P}}H$$

2. Synthesis by the Friedel–Crafts method

The synthesis of aryldichlorophosphines by a Friedel–Crafts reaction can be found in *Organic Syntheses* (10). A recent discovery has shown that this procedure can be used to prepare certain diarylphosphine oxides (32). In addition to the aryl phosphonous dichloride produced

$$ArH + PCl_3 \xrightarrow{AlCl_3} ArPCl_2\cdot AlCl_3 + HCl$$
$$ArPCl_2\cdot AlCl_3 + POCl_3 \rightarrow ArPCl_2 + AlCl_3\cdot POCl_3$$

in the reaction, two crystalline compounds were isolated from the $AlCl_3\cdot POCl_3$ complex, one acidic (the diarylphosphinic acid) and the other neutral (the diarylphosphine oxide). The corresponding diarylphosphine oxide was formed in good yield when the aryl function was mesityl, duryl, or pentamethylphenyl. With ethylbenzene the corresponding phosphinic acid was the only secondary product. In all cases the phosphinic acid was thought to result from hydrolysis and oxidation of the intermediate phosphinous chloride, R_2PCl. That the corresponding phosphinous chlorides of the highly substituted hydrocarbons are preferentially coprecipitated with the $AlCl_3\cdot POCl_3$ complex is somewhat peculiar. Obviously the reaction must be extended before an estimate can be made of its value as a preparatory method for diarylphosphine oxides.

3. Miscellaneous

(a) Synthesis by use of lithium aluminum hydride

Reduction of phosphinyl halides by means of lithium aluminum hydride appears to be a rather clean method for the preparation of dialkylphosphine oxides (106). The reaction is performed near 0°C. and with an excess of reducing agent. The chief limitation to the method is probably the availability of phosphinic acids, which are the precursors of the phosphinyl halides.

$$R_2\overset{O}{\overset{\uparrow}{P}}Cl + LiAlH_4 \rightarrow R_2\overset{O}{\overset{\uparrow}{P}}H$$

(b) Synthesis by oxidation of disubstituted phosphines

A limited amount of experimental data is available on the oxidation of secondary phosphines to secondary phosphine oxides. A recent publication includes a review of the early research (96). A solution of di(*n*-butyl)-phosphine in isopropyl alcohol treated with air at 70°C. gave di(*n*-butyl)phosphine oxide (96). Similarly, di(*n*-octyl)phosphine oxide and bis(2-cyanoethyl)phosphine oxide were obtained in unspecified yields. A secondary phosphine oxide can be converted to the corresponding phosphinic acid under oxidative conditions; this is undoubtedly one of the undesirable features in the oxidation of secondary phosphines to the oxides.

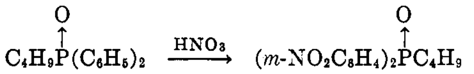
III. Reactivity of Phosphine Oxides

A. MISCELLANEOUS REACTIONS OF TERTIARY PHOSPHINE OXIDES

There has been no comprehensive study of reactions which involve alkyl groups attached directly to the phosphorus atom in tertiary phosphine oxides. Actually, Kosolapoff's review contains only a few references to investigations in this area (69). To be sure, this field looks ripe for research. This section will deal primarily with phosphine oxides which contain at least one aryl group, as they have been examined more closely in the past decade.

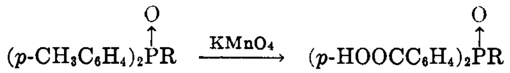
1. Aryl-substituted tertiary phosphine oxides *($ArRR'P \rightarrow O$; R and R' may be alkyl or aryl)*

Nitration of triphenylphosphine oxide resulted in formation of the corresponding *m*-nitrophenyl derivative as expected (15). Proof of structure was accomplished through synthesis of the nitro compound by an alternative route. Tribenzylphosphine oxide was converted to the *p*-nitrophenyl derivative (14). Thus, it is suggested that the phosphoryl group ($P \rightarrow O$) is similar to a carbonyl function in that both are powerful electron-withdrawing groups. A recent review discusses the influence of this group in reactions of other organophosphorus compounds (22). Butyldiphenylphosphine oxide has been reported to give the *m*-dinitro derivative in 68.4 per cent yield (89), but the structure was not proven by independent synthesis.


$$C_4H_9\overset{\overset{O}{\uparrow}}{P}(C_6H_5)_2 \xrightarrow{HNO_3} (m\text{-}NO_2C_6H_4)_2\overset{\overset{O}{\uparrow}}{P}C_4H_9$$

Another example of aromatic substitution in this series occurred when bis(chloromethyl)phenylphosphine oxide was nitrated to give the *m*-nitrophenyl derivative (108). The scarcity of papers dealing with substitution reactions on aryl groups attached to phosphorus in tertiary phosphine oxides may be due to the fact that the substituted compounds have usually been prepared by one of the synthetic methods previously described.

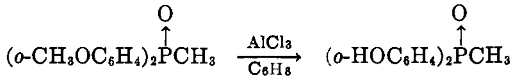
Oxidation of alkyl side chains on aryl groups of tertiary phosphine oxides can be accomplished without affecting the phosphoryl function or a carbon–phosphorus link (87). Bis(*p*-carboxyphenyl)methylphosphine oxide was obtained in 88 per cent yield by oxidation of the corresponding *p*-tolyl compound. When R was


$$(p\text{-}CH_3C_6H_4)_2\overset{\overset{O}{\uparrow}}{P}R \xrightarrow{KMnO_4} (p\text{-}HOOCC_6H_4)_2\overset{\overset{O}{\uparrow}}{P}R$$

ethyl, the corresponding acid was isolated in 82 per cent of the theoretical amount.

Tri(*o*-methoxyphenyl)phosphine oxide and di(*o*-methoxyphenyl)methylphosphine oxide, in the presence of aluminum chloride, were converted to their respective phenol derivatives in good yields (66). Cleavage of a carbon–phosphorus bond was not observed in either of these reactions.

$$(o\text{-}CH_3OC_6H_4)_3P \rightarrow O \xrightarrow[C_6H_6]{AlCl_3} (o\text{-}HOC_6H_4)_3P \rightarrow O$$


$$(o\text{-}CH_3OC_6H_4)_2\overset{\overset{O}{\uparrow}}{P}CH_3 \xrightarrow[C_6H_6]{AlCl_3} (o\text{-}HOC_6H_4)_2\overset{\overset{O}{\uparrow}}{P}CH_3$$

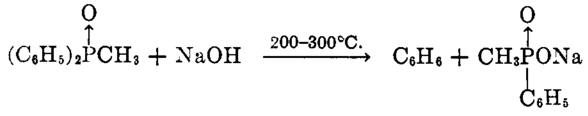
It is apparent that an enormous number of interesting derivatives are possible with tertiary phosphine oxides which possess at least one aryl function. Perhaps early difficulties encountered in the preparation of unsymmetrical tertiary phosphine oxides caused this phase of organophosphorus chemistry to remain practically untouched.

2. Cleavage of the carbon–phosphorus bond in tertiary phosphine oxides

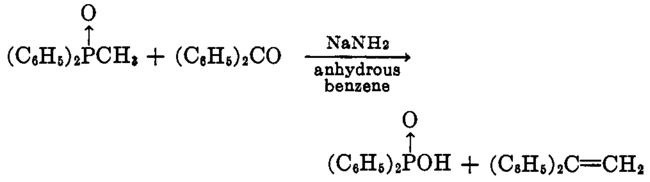
Cleavage of carbon–phosphorus bonds has been reviewed elsewhere (32, 33), but very few actual examples have been reported. Such bonds are comparable in strength to carbon–carbon bonds; this is the reason why tertiary phosphine oxides can withstand nitration mixtures and powerful oxidative conditions without suffering rupture of the carbon–phosphorus link (33). Under proper circumstances, however, tertiary phosphine oxides can undergo this type of degradation. When di(*p*-tolyl)ethylphosphine oxide was heated with water in a sealed tube at 245°C., the aqueous washings of the tube were more acidic than aqueous washings of a similar quantity of the oxide (87). Also the contents of the flask smelled of a phosphine. No further investigation of products was reported, although it is probable that bond severance occurred to produce phosphorus acids.

In a similar experiment tris(trifluoromethyl)phosphine oxide was placed in a sealed tube at room temperature with aqueous sodium hydroxide (92). The sodium salt of trifluoromethylphosphonic acid was obtained. Bis(trifluoromethyl)phosphinic acid formed when water was added instead of aqueous sodium hydroxide. The powerful inductive effect of the fluorine atoms may weaken the carbon–phosphorus linkage so that it is easily severed.

Cleavage of a carbon–phosphorus bond in the presence of base has been observed with a variety of other tertiary phosphine oxides (44, 52, 53). Fusion of tertiary phosphine oxides with sodium hydroxide was found to yield a hydrocarbon and a phosphinic acid (53). Yields of various phosphinic acids ranged from 80 to 100 per cent. A typical example is shown in the equation. It was


$$(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}CH_3 + NaOH \xrightarrow{200\text{–}300°C.} C_6H_6 + CH_3\underset{\underset{C_6H_5}{|}}{\overset{\overset{O}{\uparrow}}{P}}ONa$$

also discovered that an unusual reaction occurred when tertiary phosphine oxides which had an active methylene group attached to the phosphorus atom were allowed to react with ketones in the presence of a condensing agent (52). Both the phosphinic acid and the olefin were reported to form in high yields. The reaction probably has wider application, since a phosphonate ester, namely, diethyl benzylphosphonate, was found to undergo a similar reaction with benzophenone to give triphenylethylene as one of the products.



$$(C_6H_5)_2\overset{O}{\overset{\uparrow}{P}}CH_3 + (C_6H_5)_2CO \xrightarrow[\text{anhydrous benzene}]{NaNH_2} (C_6H_5)_2\overset{O}{\overset{\uparrow}{P}}OH + (C_6H_5)_2C{=}CH_2$$

A study of the mechanism involved in the rupture of the carbon–phosphorus linkages in tertiary phosphine oxides has not yet been reported. The proximity of electron-withdrawing groups on substituents and the basicity of the condensing agent may be factors which influence the severance of this type of chemical bond.

3. *Reduction of phosphine oxides*

Reduction of tertiary phosphine oxides to the corresponding tertiary phosphines is possible with lithium aluminum hydride or calcium aluminum hydride (46). Colored addition products were formed when the reaction was attempted with sodium in a hydrocarbon solvent (47). The yields of phosphines were higher with lithium aluminum hydride than with the calcium compound. Some limitations were observed, however. Although trialkylphosphine oxides were readily reduced, the aryl derivatives suffered a different fate. For example, triphenylphosphine oxide was converted to diphenylphosphine. Similar results were reported to occur with other arylphosphine oxides. No mention was made of an attempt to reduce mixed oxides of the type indicated in the formula below.

$$R_3P{\rightarrow}O \xrightarrow[\text{dioxane}]{LiAlH_4} R_3P$$

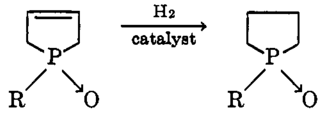
R = alkyl.

$$ArRR'P{\rightarrow}O$$

Ar = aryl; R = alkyl; R′ = alkyl or aryl.

It should be noted that Collie and Reynolds were the first to report the reduction of tertiary phosphine oxides by means of mercury–sodium amalgam (19). The experimental conditions were poorly outlined.

Raney nickel, palladium, or platinum can be used to reduce (under pressure) the double bond in a series of 1-substituted phospha-3-cyclopentene *P*-oxides (56, 77). The isolation of phosphines was not reported, a result which may indicate that the phosphoryl group is inert under the conditions of the reaction.



4. *Miscellaneous*

(a) Formation of complexes

Tertiary phosphine oxides undergo condensation with alkali metals to form dark-colored addition compounds which are sensitive to air and moisture. The color depends somewhat on the metal content of the complexes (45, 47). Several ethers were used as solvents, including tetrahydrofuran which was discovered to form a blue color with tri(biphenyl)phosphine oxide in the absence of any metal. The true identity of these adducts is unknown.

Trimethylphosphine oxide can be an acceptor for electron-deficient groups such as BF_3, SO_3, and SO_2 (11). The boron trifluoride adduct was produced in 47 per cent of theoretical quantity. It is stable in a vacuum, soluble in water, lowers the freezing point of water by three times the expected amount, and melts at 149°C. The data suggest that the phosphorus–oxygen bond is highly polarized, and the electronic charge on the oxygen atom may be of considerable magnitude.

Tertiary phosphine oxides have been reported to form stable complexes with zinc chloride (69, 87, 93). The exact ratio of zinc chloride to phosphine oxide in the complex has not been established.

A series of stable complexes composed of tertiary phosphine oxides and certain inorganic coördination compounds has been recorded recently (60).

Tridecyl- and trioctylphosphine oxides have been useful in the extraction of uranium (104).

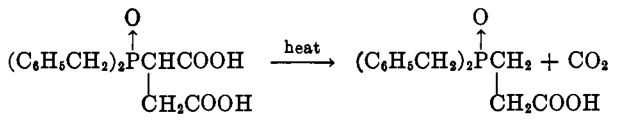
(b) Formation of phosphine dihalides

The formation of dihalides via the corresponding phosphine oxide has been described elsewhere (69). This reaction is somewhat trivial, as the chief use of the dihalide derivatives occurs in the synthesis of tertiary phosphine oxides.

$$R_3P{\rightarrow}O + PCl_5 \rightarrow R_3PCl_2 + POCl_3$$

(c) Reactions involving dialkyl α-hydroxyalkylphosphine oxides

As mentioned previously, tertiary phosphine oxides resulted when secondary phosphine oxides were treated with α,β-saturated amides, esters, ketones, and nitriles (84, 86, 96) in the presence of a base. An example is 2-dibenzylphosphinylsuccinic acid (XIV), obtained in 92 per cent yield. This acid lost carbon dioxide when heated to its melting point (84). Thus, the existence of the phosphoryl group in the molecule did not prevent the expected decarboxylation. This is another example

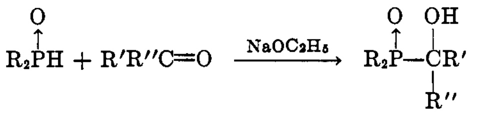


$$(C_6H_5CH_2)_2\overset{\overset{O}{\uparrow}}{P}\underset{CH_2COOH}{CHCOOH} \xrightarrow{\text{heat}} (C_6H_5CH_2)_2\overset{\overset{O}{\uparrow}}{P}\underset{CH_2COOH}{CH_2} + CO_2$$

XIV

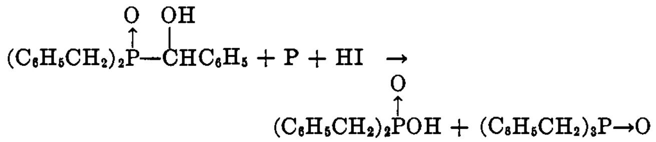
of the thermal stability of carbon–phosphorus bonds in tertiary phosphine oxides.

Addition compounds formed in the reaction of secondary phosphine oxides with aldehydes and ketones are not thermally stable (86). Preparations of the tertiary phosphine oxides (general formula XV) will be discussed in the section concerned with reactions of secondary phosphine oxides. Nearly all of these compounds (XV) suffered a depression in melting point if dried under vacuum at 100°C. (86). Cleavage occurred in an acidic or basic medium to produce the corresponding dialkylphosphinic acid. Reduction of the hydroxyl group in α-(dibenzylphosphinyl)benzyl alcohol was possible by the use of 48.3 per cent hydriodic acid and red phosphorus in glacial acetic acid. Tribenzylphosphine oxide was formed along with dibenzylphosphinic acid, as illustrated in the equation. Thus, the type of tertiary phosphine oxide represented by formula XV has not inherited the property of thermal stability which is so characteristic of many oxides.



$$R_2\overset{\overset{O}{\uparrow}}{P}H + R'R''C{=}O \xrightarrow{NaOC_2H_5} R_2\overset{\overset{O}{\uparrow}}{P}{-}\overset{\overset{OH}{|}}{\underset{\underset{R''}{|}}{C}}R'$$

XV

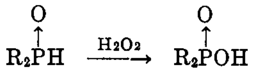


$$(C_6H_5CH_2)_2\overset{\overset{O}{\uparrow}}{P}{-}\overset{\overset{OH}{|}}{C}HC_6H_5 + P + HI \rightarrow (C_6H_5CH_2)_2\overset{\overset{O}{\uparrow}}{P}OH + (C_6H_5CH_2)_3P{\rightarrow}O$$

B. REACTIONS OF SECONDARY PHOSPHINE OXIDES

1. Oxidation

Oxidation of secondary phosphine oxides leads to the formation of phosphinic acids (32, 58, 84, 105–107). Hydrogen peroxide (30 per cent) has been used successfully to oxidize lower members of the series of di(n-alkyl)phosphine oxides (107). As the molecular weight of the oxides increased, the reaction was more sluggish, di(n-octadecyl)phosphine oxide being inert. In this example, however, the two reactants are mutually insoluble and this may account for a negative result.

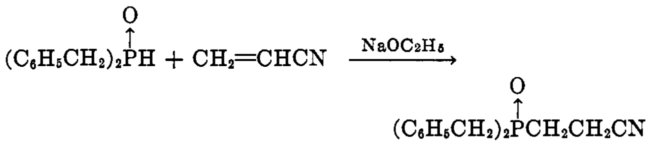


$$R_2\overset{\overset{O}{\uparrow}}{P}H \xrightarrow{H_2O_2} R_2\overset{\overset{O}{\uparrow}}{P}OH$$

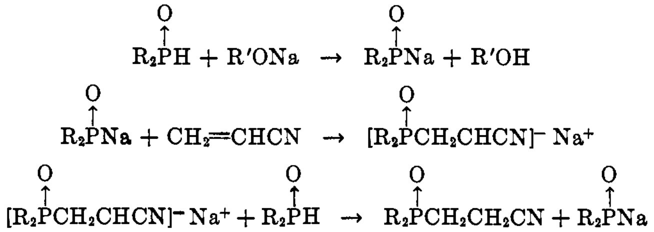
Diarylphosphine oxides have been oxidized to the corresponding diarylphosphinic acids with hydrogen peroxide (58, 105). Exceptions are dimesitylphosphine oxide, didurylphosphine oxide, and dipentamethylphenylphosphine oxide, which could be recovered almost quantitatively when treated with alkaline hydrogen peroxide (32). Although alkaline permanganate was too vigorous an oxidizing medium, alkaline ferricyanide converted dimesitylphosphine oxide to dimesitylphosphinic acid in 30 min.; the yield was nearly quantitative (32). The duryl analog required 2 hr. for complete oxidation under the same conditions, while the pentamethylphenyl compound was only 14 per cent oxidized in 17 hr. Perhaps by their very bulky nature these hydrocarbon groups give some protection to the phosphorus atom. It would be of interest to see if the proton on the phosphorus atom in this series is as active as it is in many simpler secondary phosphine oxides with regard to reactions involving additions to unsaturated materials.

2. Addition to unsaturated compounds

Secondary phosphine oxides can be added to a wide variety of unsaturated compounds (83, 86, 96). For example, in the presence of catalytic amounts of sodium ethoxide, dibenzylphosphine oxide condensed with acrylonitrile to give 3-dibenzylphosphinylpropionitrile in 66 per cent yield. Moreover, additions to α,β-unsaturated amides, esters, and ketones were observed. A base-catalyzed chain mechanism, similar to that suggested for the analogous reactions with dialkyl phosphonates (94), has been proposed (84).



$$(C_6H_5CH_2)_2\overset{\overset{O}{\uparrow}}{P}H + CH_2{=}CHCN \xrightarrow{NaOC_2H_5} (C_6H_5CH_2)_2\overset{\overset{O}{\uparrow}}{P}CH_2CH_2CN$$

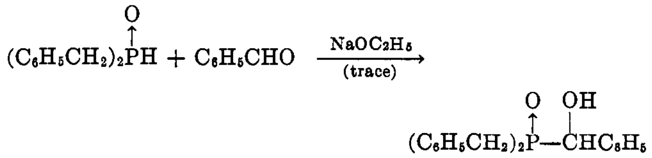


$$R_2\overset{\overset{O}{\uparrow}}{P}H + R'ONa \rightarrow R_2\overset{\overset{O}{\uparrow}}{P}Na + R'OH$$

$$R_2\overset{\overset{O}{\uparrow}}{P}Na + CH_2{=}CHCN \rightarrow [R_2\overset{\overset{O}{\uparrow}}{P}CH_2CHCN]^- Na^+$$

$$[R_2\overset{\overset{O}{\uparrow}}{P}CH_2CHCN]^- Na^+ + R_2\overset{\overset{O}{\uparrow}}{P}H \rightarrow R_2\overset{\overset{O}{\uparrow}}{P}CH_2CH_2CN + R_2\overset{\overset{O}{\uparrow}}{P}Na$$

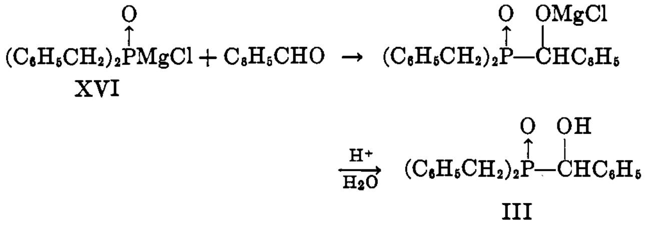
Ketones, aldehydes, and anils condensed with dialkylphosphine oxides in the presence of a trace of basic catalyst to give dialkyl phosphinyl alcohols (83, 86, 96). A general reaction with benzaldehyde will illustrate.



$$(C_6H_5CH_2)_2\overset{\overset{O}{\uparrow}}{P}H + C_6H_5CHO \xrightarrow[\text{(trace)}]{NaOC_2H_5} (C_6H_5CH_2)_2\overset{\overset{O}{\uparrow}}{P}{-}\overset{\overset{OH}{|}}{C}HC_6H_5$$

III

An interesting discovery encountered was that α-(dibenzylphosphinyl)benzyl alcohol (III) could be realized via an alternative route. Benzaldehyde was added to the Grignard complex of dibenzylphosphine oxide as shown in the equation. There is no experimental evidence to confirm the structure assigned to the chloromagnesium



$$(C_6H_5CH_2)_2\overset{O}{\overset{\uparrow}{P}}MgCl + C_6H_5CHO \rightarrow (C_6H_5CH_2)_2\overset{O}{\overset{\uparrow}{P}}-\overset{OMgCl}{\overset{|}{C}}HC_6H_5$$

XVI

$$\xrightarrow[H_2O]{H^+} (C_6H_5CH_2)_2\overset{O}{\overset{\uparrow}{P}}-\overset{OH}{\overset{|}{C}}HC_6H_5$$

III

salt (XVI), although a similar type of complex has been postulated to form with dialkyl phosphonates; this complex also condensed with aldehydes and ketones (36).

3. Conversion to phosphinyl halides

Phosphinyl chlorides can be prepared directly from secondary phosphine oxides. Chlorine gas (106), thionyl chloride (58), and *N*-chlorosuccinimide (58) have been used for this purpose. The chief value of this reaction

$$R_2\overset{O}{\overset{\uparrow}{P}}H \xrightarrow{SOCl_2} R_2\overset{O}{\overset{\uparrow}{P}}Cl$$

has been for proof of structure of the secondary phosphine oxides, since hydrolysis of the phosphinyl halides leads to phosphinic acids. Phosphinic acids were prepared also by the oxidation of secondary phosphine oxides.

IV. PHYSICAL PROPERTIES AND STRUCTURE

A. PHOSPHINE OXIDES

1. General properties

Tertiary phosphine oxides are for the most part a class of compounds of extreme stability. Strong alkali can cause rupture of the carbon–phosphorus bond, with the most electronegative group being eliminated (53). This reaction should be considered somewhat exceptional, however, since heating to the melting point and strong oxidizing media generally do not affect the carbon–phosphorus linkage.

Tertiary phosphine oxides are often solids at room temperature and frequently soluble in alcohol and other organic solvents. The formation of hydrates, many of which are quite stable, is a common occurrence. Drying in vacuum near 100°C. over strong desiccants is a procedure sometimes used successfully to release the tertiary phosphine oxide from its hydrate. Many oxides have high boiling points and long liquid ranges.

The bond-dissociation energy of the phosphorus–oxygen link has been determined for two tertiary phosphine oxides (16). Heats of oxidation by hydrogen peroxide (in methanol) of the corresponding phosphines were used to calculate the dissociation energies. The values derived for tripropylphosphine oxide and tributylphosphine oxide were 138.3 kcal. per mole and 137.2 kcal. per mole, respectively. A figure of 150.8 kcal. per mole was found for the phosphorus–oxygen bond in triethyl phosphate. In view of the numerical values obtained for the three compounds, it was suggested that the group attached to phosphorus probably influences the dissociation process. There appears to be a need for additional thermochemical studies on a large number of oxides before a correlation between the dissociation energy and the nature of the phosphorus–oxygen bond can be made.

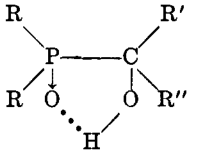
2. Absorption spectra and nuclear magnetic resonance data

A comprehensive study of the ultraviolet absorption spectra of tertiary phosphine oxides has not been published. The spectrum of triphenylphosphine has been recorded and compared with that of triphenylphosphine oxide (61, 62). Some interaction between the phenyl groups and phosphorus was detected in the spectrum of triphenylphosphine. Since no unshared pair of valence electrons exists on the phosphorus atom of triphenylphosphine oxide, it was not surprising that its spectrum indicated that each phenyl group made an individual contribution to the molecular extinction coefficient. This does not preclude the existence, in certain tertiary phosphine oxides, of an interaction between the phosphorus atom and aryl substituents which contain powerful electron-donating groups. An investigation has not been published on this subject.

There are several reports concerned with the infrared spectra of organophosphorus compounds (6, 7, 8, 21, 25, 26, 37, 92), but only a few tertiary phosphine oxides are included. Intense bands at 1190 cm.$^{-1}$ and 1176 cm.$^{-1}$ were noted for the phosphoryl group in triphenylphosphine oxide and trimethylphosphine oxide, respectively. A shift of the phosphoryl peak (1326 cm.$^{-1}$) in tris-(trifluoromethyl)phosphine oxide (92) may be caused by the fluorine atoms, the inductive effect of which could increase the force constant of the phosphorus–oxygen bond. Although absorption near 1440 cm.$^{-1}$ has been fairly well established for the phosphorus–phenyl linkage (25), no good correlations exist for alkyl-substituted tertiary phosphine oxides, with perhaps one exception. A band at 750 cm.$^{-1}$ has been assigned to the stretching of the carbon–phosphorus bond in trimethylphosphine oxide (21, 26).

Since tertiary phosphine oxides are quite often hygroscopic, a band for water is usually evident in the infrared spectra. The solid-phase spectrum of triphenylphosphine oxide indicates intramolecular bonding between the phosphoryl function and phenyl groups which might account for the presence of a peak in the area where hydrogen bonding occurs (37). Dipole–dipole attraction was predicted in solid tri(*n*-octyl)phosphine oxide as the phosphoryl group absorbed at 1142 cm.$^{-1}$, while in solution the peak was at 1170 cm.$^{-1}$

The infrared spectra of dialkyl α-hydroxyalkylphosphine oxides indicate intramolecular association between the phosphoryl groups and the hydroxyl functions (85). Absorption at 3050–3100 cm.$^{-1}$ on the crystalline compounds did not shift significantly (3050–3090 cm.$^{-1}$) in carbon disulfide solution even with dilutions up to 0.01 M. Deuteration of di(n-octyl) α-hydroxybenzylphosphine oxide produced a compound which had an O-D band (2337 cm.$^{-1}$) in its infrared spectrum. The data point to hydrogen bonding of the type shown in the formula.



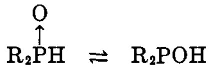
In the solid state these compounds displayed absorption in the infrared for the phosphoryl group at 1100–1140 cm.$^{-1}$; a shift to 1160–1165 cm.$^{-1}$ was observed in carbon disulfide.

Nuclear magnetic resonance as a tool in organophosphorus chemistry has been investigated to some extent, but a very small number of tertiary phosphine oxides have been included in the studies (13, 41, 42, 90, 102). A qualitative observation indicates that larger variations in chemical shifts occur with trisubstituted phosphorus compounds than with tetrasubstituted species (102). The chemical shift seems to depend upon the nature of the atoms attached to phosphorus, but a quantitative study of this type has never been reported for a variety of substituted tertiary phosphine oxides.

B. SECONDARY PHOSPHINE OXIDES

1. General properties

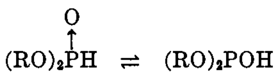
A point of controversy with regard to the structure of secondary phosphine oxides has been concerned with the possible existence of an equilibrium as depicted in the equation.



$$R_2\overset{\overset{O}{\uparrow}}{P}H \rightleftharpoons R_2POH$$

XVII XVIII

Dialkyl phosphonates could exhibit a similar equilibrium. Potentiometric titrations have shown that the



$$(RO)_2\overset{\overset{O}{\uparrow}}{P}H \rightleftharpoons (RO)_2POH$$

secondary phosphine oxides are neutral (107). The research of Hunt and Saunders revealed that an equilibrium between compounds XVII and XVIII does exist. They were able to prepare the silver salt of diphenylphosphinous acid in nearly quantitative yield (58). The formation of the salt is slow, which implies that the equilibrium may be far to the left. An interesting study might be to examine the effect on the equilibrium when various substituents were attached to the aromatic rings of diarylphosphine oxides.

Secondary phosphine oxides are relatively unstable and tend to decompose when heated at their melting points or when dried at 100°C. in vacuum (107). This is in sharp contrast to the behavior of most tertiary phosphine oxides. In the presence of alkali secondary phosphine oxides are converted to the alkali salt of the corresponding disubstituted phosphinic acid. Many of the dialkylphosphine oxides can be oxidized to the dialkyl phosphinic acids, as previously described (107). Certain diarylphosphine oxides with bulky aryl groups are more difficult to oxidize, presumably owing to steric hindrance (32).

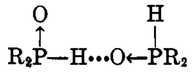
The di(n-alkyl)phosphine oxides from C_6 to C_{18} are white solids (107), as are diphenylphosphine oxide (58), didurylphosphine oxide, and dipentamethylphenylphosphine oxide (32). The lower dialkyl members were thought at one time to be too unstable to exist, but di(n-butyl)phosphine oxide has been reported recently (96). A plot of the melting points of the di(n-alkyl)phosphine oxides versus the number of carbon atoms in an alkyl group shows a steady increase in melting point with increasing chain length (107).

Hydrocarbons have been used as solvents to recrystallize dialkylphosphine oxides (106, 107). The diarylphosphine oxides prepared by Frank were soluble in benzene and alcohol; they were insoluble in water. No record has been published that secondary phosphine oxides form hydrates.

2. Absorption spectra and nuclear magnetic resonance data

The ultraviolet absorption spectra of secondary phosphine oxides have not been recorded in the literature.

No systematic study of the infrared spectra of secondary phosphine oxides exists. The known dialkylphosphine oxides are reported to have strong absorption in the infrared near 1190 cm.$^{-1}$ (P→O) and 2283 cm.$^{-1}$ (P—H) in carbon disulfide (85). These peaks were found at 1150–1155 cm.$^{-1}$ and near 2335 cm.$^{-1}$, respectively, when the infrared spectra were determined on the crystalline solids. An intermolecular association has been postulated for the shift in frequency of the phosphoryl group.



$$R_2\overset{\overset{O}{\uparrow}}{P}\text{—}H\cdots O\leftarrow\overset{\overset{H}{|}}{P}R_2$$

A conspicuous absentee in the spectra determined in carbon disulfide was a band for the hydroxyl function (85).

The few diarylphosphine oxides reported appear to exhibit doublets for the absorption of the phosphoryl function (32, 107). For example, didurylphosphine oxide had peaks at 1160 cm.$^{-1}$ and 1190 cm.$^{-1}$, both of which were assigned to the phosphoryl group (32). The phosphorus–hydrogen bond in these diaryl derivatives

TABLE 1

Tertiary phosphine oxides

$RR'R''P \rightarrow O$

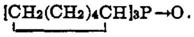
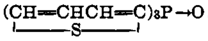
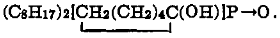
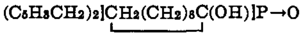
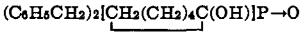
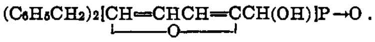
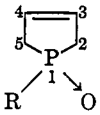
Compound	Boiling Point	Melting Point	References
$R = R' = R'' =$ alkyl			
	°C.	*°C.*	
$(CF_3)_3P \rightarrow O$	23.6		(92)
$(CH_2=CHCH_2)_3P \rightarrow O$	98/0.5 mm.	15–17	(65)
$[(CH_3)_2CHCH_2]_3P \rightarrow O$		123–125	(100)
$[CH_3(CH_2)_3CH(C_2H_5)CH_2]_3P \rightarrow O$	205–213/2–3 mm.		(9)
$[(CH_3)_3CCH_2CH(CH_3)CH_2CH_2]_3P \rightarrow O$	185–190/0.1 mm.		(9)
 $[\underbrace{CH_2(CH_2)_4CH}]_3P \rightarrow O$		155–157	(59)
$(C_8H_{17})_3P \rightarrow O$	201–202/1 mm.	51–51.5	(9, 104)
$(C_{10}H_{21})_3P \rightarrow O$	278–283/3–4 mm.	40–42	(9)
$(C_{12}H_{25})_3P \rightarrow O$	235–240/0.1 mm.	44–48	(9)
$(NCCH_2CH_2)_3P \rightarrow O$		172–173	(95)
$(HOOCCH_2CH_2)_3P \rightarrow O$		155–156	(95)
$(C_6H_5CH_2CH_2)_3P \rightarrow O$		150–152	(9)
$(C_6H_5CH_2CH_2CH_2)_3P \rightarrow O$		84–85	(9)
$R = R' = R'' =$ aryl (or heterocyclic)			
$(p\text{-}HOOCC_6H_4)_3P \rightarrow O$		323–330	(87)
$(o\text{-}CH_3COOC_6H_4)_3P \rightarrow O$		197–199	(66)
$(p\text{-}CH_3OOCC_6H_4)_3P \rightarrow O$		123–125	(87)
$[p\text{-}(CH_3)_2NC_6H_4]_3P \rightarrow O$		305–306	(97)
$(o\text{-}HOC_6H_4)_3P \rightarrow O$		214.5–216	(66)
$(o\text{-}CH_3OC_6H_4)_3P \rightarrow O$		216–217	(27)
$(2\text{-}C_{10}H_7)_3P \rightarrow O$		248–249	(12)
Tri(9-phenanthryl)phosphine oxide		354–356	(81, 82)
Tris(1,2-benzanthr-10-yl)phosphine oxide		191–193	(81, 82)
 $(\underbrace{CH=CHCH=C}_{S})_3P \rightarrow O$		129–130	(12)
$R = R' \neq R''$ $R = R' =$ alkyl; $R'' =$ alkyl			
$(C_2H_5)_2(C_4H_9)P \rightarrow O$	85.5–86/1 mm.		(4)
$(C_2H_5)_2(C_2H_5OOCCH_2)P \rightarrow O$	113–113.5/3 mm.		(4)
$(NCCH_2CH_2)_2[CCl_3CH(OH)]P \rightarrow O$		159–160	(96)
$(C_4H_9)_2[CCl_3CH(OH)]P \rightarrow O$		132–133	(96)
$(C_8H_{17})_2(NCCH_2CH_2)P \rightarrow O$		53.4–54.2	(84, 96)
$(C_8H_{17})_2(HOOCCH_2CH_2)P \rightarrow O$		81.5–82.1	(84)
$(C_8H_{17})_2(NH_2COCH_2CH_2)P \rightarrow O$		132.6–133	(84)
$(C_8H_{17})_2[HOOCCH_2CH(COOH)]P \rightarrow O$		97.5–99	(84)
$(C_8H_{17})_2[(CH_3)_2C(OH)]P \rightarrow O$		54.5–56	(86)
 $(C_8H_{17})_2[\underbrace{CH_2(CH_2)_4C}(OH)]P \rightarrow O$		67.5–68.1	(86)
$(C_6H_5CH_2)_2(CH_3)P \rightarrow O$		133.5–134	(5)
$(C_6H_5CH_2)_2(NCCH_2CH_2)P \rightarrow O$		109–110	(84)
$(C_6H_5CH_2)_2(HOOCCH_2CH_2)P \rightarrow O$		180.6–181.4	(84)
$(C_6H_5CH_2)_2(CH_3OOCCH_2CH_2)P \rightarrow O$		122.4–123	(84)
$(C_6H_5CH_2)_2(C_2H_5OOCCH_2CH_2)P \rightarrow O$		93–93.6	(84)
$(C_6H_5CH_2)_2(NH_2COCH_2CH_2)P \rightarrow O$		195–195.6	(84)
$(C_6H_5CH_2)_2[NCCH(CH_3)CH_2]P \rightarrow O$		121.5–122	(84)
$(C_6H_5CH_2)_2[HOOCCH(CH_3)CH_2]P \rightarrow O$		142.5–143	(84)
$(C_6H_5CH_2)_2[C_2H_5OOCCH(CH_3)CH_2]P \rightarrow O$		92.7–93.1	(84)
$(C_6H_5CH_2)_2[NCCH_2(CH_3)CH]P \rightarrow O$		93.5–94.1	(84)
$(C_6H_5CH_2)_2[HOOCCH_2CH(CH_3)]P \rightarrow O$		151–151.8	(84)
$(C_6H_5CH_2)_2[HOOCCH_2CH(COOH)]P \rightarrow O$		218–218.5 (d.)	(84)
$(C_6H_5CH_2)_2[CH_3CH(OH)]P \rightarrow O$		153.7–154	(86)
$(C_6H_5CH_2)_2[C_2H_5CH(OH)]P \rightarrow O$		165.8–166.4	(86)
$(C_6H_5CH_2)_2[(CH_3)_2C(OH)]P \rightarrow O$		144.5–145.5	(86)
$(C_6H_5CH_2)_2[C_3H_7CH(OH)]P \rightarrow O$		169.1–169.8	(86)
$(C_6H_5CH_2)_2[(CH_3)_2CHCH(OH)]P \rightarrow O$		175–175.6	(86)
$(C_6H_5CH_2)_2[(C_2H_5)(CH_3)C(OH)]P \rightarrow O$		153.5–154	(86)
 $(C_6H_5CH_2)_2[\underbrace{CH_2(CH_2)_3C}(OH)]P \rightarrow O$		184.3–185	(86)
 $(C_6H_5CH_2)_2[\underbrace{CH_2(CH_2)_4C}(OH)]P \rightarrow O$		170–170.6	(86)
 $(C_6H_5CH_2)_2[\underbrace{CH=CHCH=C}_{O}CH(OH)]P \rightarrow O$		170.8–171.7	(86)

TABLE 1—*Continued*

Compound	Boiling Point	Melting Point	References
R = R′ ≠ R″ R = R′ = alkyl; R″ = alkyl (contains an aryl group in the chain)			
	°C.	*°C.*	
$(C_8H_{17})_2[CH_3COCH_2CH(C_6H_5)]P \rightarrow O$		62.3–63	(84)
$(C_8H_{17})_2[C_6H_5CH(OH)]P \rightarrow O$		62.5–64	(86)
$(C_8H_{17})_2[o\text{-}ClC_6H_4CH(OH)]P \rightarrow O$		97.5–98.1	(86)
$(C_8H_{17})_2[o\text{-}O_2NC_6H_4CH(OH)]P \rightarrow O$		122.2–122.6	(86)
$(C_6H_5CH_2)_2[HOOCCH_2CH(C_6H_5)]P \rightarrow O$		211–212	(84)
$(C_6H_5CH_2)_2[CH_3OOCCH_2CH(C_6H_5)]P \rightarrow O$		178.2–178.6	(84)
$(C_6H_5CH_2)_2[C_2H_5OOCCH_2CH(C_6H_5)]P \rightarrow O$		138.5–139	(84)
$(C_6H_5CH_2)_2[CH_3COCH_2CH(C_6H_5)]P \rightarrow O$		171.6–172.1	(84)
$(C_6H_5CH_2)_2[C_6H_5COCH_2CH(C_6H_5)]P \rightarrow O$		205.6–206.5	(84)
$(C_6H_5CH_2)_2[C_6H_5CH(OH)]P \rightarrow O$		163.2–164	(86)
$(C_6H_5CH_2)_2[o\text{-}ClC_6H_4CH(OH)]P \rightarrow O$		173.8–174.5	(86)
$(C_6H_5CH_2)_2[p\text{-}(CH_3)_2NC_6H_4CH(OH)]P \rightarrow O$		153.6–154.2	(86)
$(C_6H_5CH_2)_2[o\text{-}HOC_6H_4CH(OH)]P \rightarrow O$		133.7–134.2	(86)
$(C_6H_5CH_2)_2[o\text{-}O_2NC_6H_4CH(OH)]P \rightarrow O$		187.1–187.5	(86)
$(C_6H_5CH_2)_2[m\text{-}O_2NC_6H_4CH(OH)]P \rightarrow O$		176.7–177	(86)
$(C_6H_5CH_2)_2[p\text{-}O_2NC_6H_4CH(OH))P \rightarrow O$		186.5–187	(86)
$(C_6H_5CH_2)_2[3,4\text{-}(—OCH_2O—)C_6H_3CH(OH)]P \rightarrow O$		195.5–196.3	(86)
R = R′ ≠ R″ R = R′ = alkyl; R″ = aryl			
$(ClCH_2)_2(C_6H_5)P \rightarrow O$		141–142	(108)
$(ClCH_2)_2(m\text{-}NH_2C_6H_4)P \rightarrow O$		110–111	(108)
$(ClCH_2)_2(m\text{-}ClC_6H_4)P \rightarrow O$		129–130	(108)
$(ClCH_2)_2(m\text{-}O_2NC_6H_4)P \rightarrow O$		155–156	(108)
$(ICH_2)_2(C_6H_5)P \rightarrow O$		172–173	(108)
$(CH_2{=}CHCH_2)_2(C_6H_5)P \rightarrow O$	143–146/0.2 mm.	48–50	(8)
$[CH_2{=}C(CH_3)CH_2]_2(C_6H_5)P \rightarrow O$	155–158/1 mm.	67–69	(8)
$(CH_3CH_2CH_2)_2(C_6H_5)P \rightarrow O$	121–124/0.5–1 mm.		(8)
$(NCCH_2CH_2)_2(C_6H_5)P \rightarrow O$		108–109	(95)
$(HOOCH_2CH_2)_2(C_6H_5)P \rightarrow O$		199–202	(95)
R = R′ ≠ R″ R = R′ = aryl; R″ = alkyl			
$(C_6H_5)_2(CH_2Cl)P \rightarrow O$	146–147/2 mm.	122–124	(63)
$(C_6H_5)_2(C_4H_9)P \rightarrow O$		95 (89.5)	(71, 89)
$(C_6H_5)_2(C_6H_{13})P \rightarrow O$		61–62	(101)
$(C_6H_5)_2[\underbrace{CH_2(CH_2)_4CH}]P \rightarrow O$		165–166	(53)
$(C_6H_5)_2(C_8H_{17})P \rightarrow O$		64–65	(101)
$(C_6H_5)_2(C_{12}H_{25})P \rightarrow O$		65–65	(53)
$(C_6H_5)_2(C_{16}H_{33})P \rightarrow O$		80	(71)
$(C_6H_5)_2(C_{18}H_{37})P \rightarrow O$		77–78	(53)
$(C_6H_5)_2[C_6H_5CH(OH)]P \rightarrow O$		178–179.5	(86)
$(p\text{-}HOOCC_6H_4)_2(CH_3)P \rightarrow O$		285	(87)
$(p\text{-}CH_3OOCC_6H_4)_2(CH_3)P \rightarrow O$		225.5	(87)
$(o\text{-}CH_2COOC_6H_4)_2(CH_3)P \rightarrow O$		201–203	(66)
$(o\text{-}HOC_6H_4)_2(CH_3)P \rightarrow O$		204.5–206	(66)
$(o\text{-}CH_3OC_6H_4)_2(CH_3)P \rightarrow O$		150	(66)
$(p\text{-}HOOCC_6H_4)_2(C_2H_5)P \rightarrow O$		265	(87)
$(p\text{-}CH_3OOCC_6H_4)_2(C_2H_5)P \rightarrow O$		162	(87)
$(p\text{-}CH_3C_6H_4)_2(C_2H_5)P \rightarrow O$		77.5	(87)
$(m\text{-}O_2NC_6H_4)_2(C_4H_9)P \rightarrow O$		124–125.5	(89)
R = R′ ≠ R″ R = R′ = aryl; R″ = aryl			
$(C_6H_5)_2(m\text{-}NH_2C_6H_4)P \rightarrow O$		160–161	(54)
$(C_6H_5)_2(p\text{-}NH_2C_6H_4)P \rightarrow O$		235	(54)
$(C_6H_5)_2(m\text{-}HOC_6H_4)P \rightarrow O$		158–160	(54)
$(C_6H_5)_2(m\text{-}CH_3OC_6H_4)P \rightarrow O$		112–113	(54)
$(C_6H_5)_2(p\text{-}CH_3OC_6H_4)P \rightarrow O$		112–113	(54)
$(C_6H_5)_2(m\text{-}CH_3C_6H_4)P \rightarrow O$		123–124	(54)
$(p\text{-}HOOCC_6H_4)_2(C_6H_5)P \rightarrow O$		335	(87)
$(p\text{-}CH_3OOCC_6H_4)_2(C_6H_5)P \rightarrow O$		165–166	(87)
$(m\text{-}CH_3C_6H_4)_2(C_6H_5)P \rightarrow O$		108.5–109	(43)
$(p\text{-}CH_3C_6H_4)_2(C_6H_5)P \rightarrow O$		81–83	(54, 87)
Di-tertiary-phosphine oxide			
$(C_6H_5)_2P(O)C{\equiv}CP(O)(C_6H_5)_2$		164	(44)

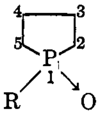
TABLE 2

1-Substituted phospha-3-cyclopentene P-oxides



R	Position and Substituent	Boiling Point	Melting Point	References
		°*C.*	°*C.*	
C_2H_5	$2 = 4 = 5 = H; 3 = CH_3$	116–117/0.6 mm.		(76)
C_6H_5	$2 = 3 = 4 = 5 = H$	139–142/0.5 mm.		(76)
C_6H_5	$2 = 4 = 5 = H; 2 = CH_3$	160–180/1 mm.		(76)
C_6H_5	$3 = 4 = 5 = H; 3 = CH_3$	160–164/0.7 mm.		(76)
C_6H_5	$3 = 5 = H; 2 = 4 = CH_3$	202–208/8 mm.		(76)
C_6H_5	$2 = 5 = H; 3 = 4 = CH_3$	173–175/0.3 mm.		(76)
C_6H_5	$2 = 4 = 5 = H; 3 = (CH_3)_2C{=}CHCH_2CH_2$	192–193/0.2 mm.		(76)
C_6H_5	$3 = 4 = 5 = H; 2 = C_6H_5$	224–226/0.9 mm.	96–98	(76)
C_6H_5	$2 = 4 = 5 = H; 3 = C_6H_5$	235–240/0.2 mm.	125	(76)
C_6H_5	$2 = 3 =$ —$(CH_2)_4$— and $4 = 5 =$ —$(CH_2)_4$—	210–220/0.5 mm.		(76)
C_6H_5	$2 = 4 = 5 = H; 3 = Cl$	158–164/0.1 mm.		(76)
C_6H_5	$2 = 4 = 5 = H; 3 = Br$	160–165/0.5 mm.		(76)
p-$CH_3OC_6H_4$	$2 = 4 = 5 = H; 3 = CH_3$	210–212/0.7 mm.		(76)

Reduction products of 1-substituted phospha-3-cyclopentene P-oxides



R	Position and Substituent	Boiling Point	References
		°*C.*	
C_2H_5	$2 = 4 = 5 = H; 3 = CH_3$	95–100/0.6 mm.	(77)
C_6H_5	$2 = 5 = H; 3 = 4 = CH_3$	160–168/0.7 mm.	(77)
C_6H_5	$2 = 4 = 5 = H; 3 = (CH_3)_2CHCH_2CH_2CH_2$	190–191/0.5 mm.	(77)
p-$CH_3OC_6H_4$	$2 = 4 = 5 = H; 3 = CH_3$	178–185/0.3 mm.	(77)

absorbs in the range previously reported for the dialkylphosphine oxides: namely, 2300–2400 cm.$^{-1}$

The structures of dialkyl phosphonates and of the analogous dialkylphosphine oxides have been a debatable subject. Nuclear magnetic resonance measurements have demonstrated that 95 per cent of the hydrogen is attached to the phosphorus atom in the phosphonates (13). This was supported by an infrared analysis (24). The assumption that this same property is characteristic of secondary phosphine oxides is probably valid in view of the supporting infrared data and chemical evidence previously described. However, a direct report concerned with nuclear magnetic resonance measurements on a series of secondary phosphine oxides could not be found.

V. TABLES OF NEW PHOSPHINE OXIDES

Table 1 lists tertiary phosphine oxides with various substituents, while table 3 contains the secondary phosphine oxides. Table 2 presents the 1-substituted phospha-3-cyclopentene *P*-oxides (and their reduction products).

TABLE 3

Secondary phosphine oxides

$RR'(H)P \rightarrow O$

Compound	Melting Point	References
$R = R' =$ alkyl		
	°*C.*	
$(C_4H_9)_2(H)P \rightarrow O$	66	(96)
$(C_5H_{11})_2(H)P \rightarrow O$	65–66 (d.)	(107)
$(C_6H_{13})_2(H)P \rightarrow O$	76.5	(106, 107)
$(C_7H_{15})_2(H)P \rightarrow O$	80.6–81.6 (d.)	(107)
$(C_8H_{17})_2(H)P \rightarrow O$	85–86	(96, 106, 107)
$(C_9H_{19})_2(H)P \rightarrow O$	88–89 (d.)	(107)
$(C_{10}H_{21})_2(H)P \rightarrow O$	91.5–92.5	(107)
$(C_{11}H_{23})_2(H)P \rightarrow O$	96–97	(107)
$(C_{12}H_{25})_2(H)P \rightarrow O$	97.2–97.8	(107)
$(C_{14}H_{29})_2(H)P \rightarrow O$	102–103	(107)
$(C_{16}H_{33})_2(H)P \rightarrow O$	106–107	(107)
$(C_{18}H_{37})_2(H)P \rightarrow O$	109–109.5	(106, 107)
$(NCCH_2CH_2)_2(H)P \rightarrow O$	98–99	(96)
$(C_6H_5CH_2)_2(H)P \rightarrow O$	109.3–110.1	(84)
$R = R' =$ aryl		
$(C_6H_5)_2(H)P \rightarrow O$	53–56	(58)
$(o\text{-}CH_3OC_6H_4)_2(H)P \rightarrow O$	135–136	(105)
$[2,3,5,6\text{-}(CH_3)_4C_6H]_2(H)P \rightarrow O$	150 (d.)	(32)
$[2,3,4,5,6\text{-}(CH_3)_5C_6]_2(H)P \rightarrow O$	240 (d.)	(32)

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