Phosphorus Mustards. III. Bis(2-chloroethyl)methylphosphine Oxide and Bis(2-benzoxyethyl)methylphosphine[1a,b]

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Bis(2-hydroxyethyl)methylphosphine hydrochloride reacts with SOCl₂ in CHCl₃ to give bis(2-chloroethyl)methyldichlorophosphorane. This reaction is considered to proceed initially *via* a cyclic transition state, with consequent transfer of oxygen from S to P, followed by chlorination of the phosphonyl group. Subsequent chlorination of the 2-hydroxyethyl groups yields the phosphorane which is rapidly hydrolyzed to bis(2-chloroethyl)methylphosphine oxide. The oxide can lose Cl⁻ due to neighboring group participation of the phosphoryl oxygen, and subsequent base-assisted proton removal results in the formation of (2-chloroethyl)methylvinylphosphine oxide. Bis(2-chloroethyl)methylphosphine oxide exhibited no "mustard-like" activity on bone marrow, but there was slight inhibition of a transplanted murine ependymoblastoma (in C3H mice) at doses of 1000 mg/kg. Bis(2-benzoxyethyl)methylphosphine appears to be devoid of mustard-like activity.

In a recent communication from this laboratory,[1b] the synthesis of bis(2-chloroethyl)methylphosphine hydrochloride (HP2·HCl, 2) was reported. However, the lack of "mustard-like" activity and the unexpectedly rapid tranformations of this product in chemical systems prompted further investigation. From this research it now appears that instead of the expected mustard, bis(2-chloroethyl)methyldichlorophosphorane (6) was the product which was actually isolated. This paper describes the experimental basis for this observation and the synthesis and biological evaluation of bis(2-benzoxyethyl)methylphosphine (3) and the phosphorus analog of nitromin, bis(2-chloroethyl)methylphosphine oxide (7).

Discussion and Chemical Results.—In the preparation of nitrogen and sulfur mustards, the final step in the reaction sequence usually involves the chlorination of 2-hydroxyethyl groups. This has been frequently accomplished by use of thionyl chloride and this reagent was used in the attempted preparation of 2.

The chemical transformations of the nitrogen analogs of such compounds are well documented[2] with the intermediate formation of the highly reactive cyclic aziridinium ion. There is ample evidence that trivalent phosphorus in such systems acts as a neighboring group in similar intramolecular displacement reactions.[3]

It has been recently postulated[4] that the phosphorus analog of the aziridinium ion, the highly labile phosphoniacyclopropane, is formed as an intermediate in the thermal decomposition of 2-substituted ethyldiphenylphosphines $(XCH_2CH_2)P(C_6H_5)_2$.

On this basis it was assumed that under aqueous conditions, the ultimate hydrolysis product of the free phosphine $CH_3P(CH_2CH_2CL)_2$ would be bis(2-hydroxyethyl)methylphosphine (1). However, the only compound isolated from the addition of oxygen-free water (in a nitrogen atmosphere) to the presumed bis-(2-chloroethyl)methylphosphine hydrochloride (2) was a low-melting, hygroscopic solid, identified as bis-(2-chloroethyl)methylphosphine oxide (7). This reaction occurs extremely rapidly as noted by changes in the nmr spectrum following the addition of deuterium oxide to a deuteriochloroform solution of 2.

This observation raised serious questions as to the validity of 2 arising from the chlorination of the hydrochloride of 1. The nature of the product obtained from this reaction is dependent upon both temperature and the molar ratio of SOCl₂ used. In order to obtain a solid product it is essential to use at least a twofold excess of SOCl₂, otherwise intractable yellow syrups and pastes are formed. This indicated that possibly the phosphorus in this hydrochloride, as well as the hydroxyl groups, was reacting with SOCl₂. In order to determine whether this were the case, tri-*n*-butylphosphine and its hydrochloride were treated with varying amounts of SOCl₂ in chloroform solution. With a phosphine–thionyl chloride molar ratio of 1:2, a highly labile solid was isolated in high yield with properties very similar to the reported HP2 hydrochloride.[1b] This is tri-*n*-butyldichlorophosphorane.[5] During the course of this reaction sulfur precipitated which was also observed in the attempted synthesis of HP2 from the phosphine hydrochloride. With a 1:1 molar ratio of reactants, only oils were obtained which showed no band in the ir which could be attributable to the phosphoryl group (P=O).[6] These oils and the solid tri-*n*-butyldichlorophosphorane reacted with oxygen-free water to form tri-*n*-butylphosphine oxide.[5] As additional support for the structure of the chlorophosphorane was the formation of tri-*n*-butylmethoxyphosphonium tetraphenylborate from the reaction of the chlorophosphorane with sodium tetraphenylborate in methanol. In contrast, tri-*n*-butylphosphine hydrochloride formed tri-*n*-butylphosphonium tetraphenylborate.

Brief mention is made by Poshkus, *et al.*,[7] that tri-

(1) (a) This research was supported by grants from the John A. Hartford Foundation, Inc., the U. S. Atomic Energy Commission (AT-(30-1) 3267), and the U. S. Public Health Service (CA-07368 and NB-04512). (b) Paper II: D. C. Smith, A. H. Soloway, and R. W. Turner, *J. Med. Chem.*, **9**, 360 (1966). (c) To whom requests for reprints should be directed: Department of Medicinal Chemistry, College of Pharmacy, Northeastern University, Boston, Mass. 02115.
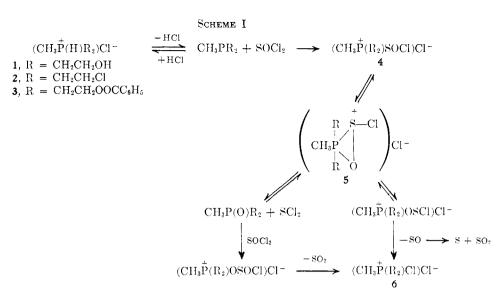
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SCHEME I

$$(CH_3\overset{+}{P}(H)R_2)Cl^- \underset{+HCl}{\overset{-HCl}{\rightleftharpoons}} CH_3PR_2 + SOCl_2 \longrightarrow (CH_3\overset{+}{P}(R_2)SOCl)Cl^-$$
$$\hspace{12cm} 4$$

1, R = CH$_2$CH$_2$OH
2, R = CH$_2$CH$_2$Cl
3, R = CH$_2$CH$_2$OOCC$_6$H$_5$

$$\left(\begin{array}{c} R \\ CH_3P \\ R \end{array} \begin{array}{c} \overset{+}{S}-Cl \\ | \\ O \end{array} \right) Cl^-$$
$$5$$

$$CH_3P(O)R_2 + SCl_2 \hspace{3cm} (CH_3\overset{+}{P}(R_2)OSCl)Cl^-$$

$$\downarrow SOCl_2 \hspace{4cm} \downarrow -SO \longrightarrow S + SO_2$$

$$(CH_3\overset{+}{P}(R_2)OSOCl)Cl^- \overset{-SO_2}{\longrightarrow} (CH_3\overset{+}{P}(R_2)Cl)Cl^-$$
$$\hspace{9cm} 6$$

phenylphosphine reacts with SOCl$_2$ to form the phosphine oxide and an oil which was presumed to be triphenyldichlorophosphorane. Horner and Nickel had also found[8] that the oxide was formed in high yield from triphenylphosphine and benzenesulfonyl chloride. Additionally there have been recent reports on the reaction of tertiary phosphines with SO$_2$[9] and with dimethyl sulfoxide.[10] However, no work has been reported previously on the oxidation of tertiary phosphine hydrohalides by such sulfur-containing compounds. Studies involving the transfer of oxygen and/or chlorine from such compound to phosphites,[11] phosphorus halides,[10] and phosphine oxides[12] have been the subject of numerous papers. The facile chlorination of these compounds and tertiary phosphines is further supported by their ability to abstract halogen from halogenated solvents under suitable conditions.[13]

In order to account for the products arising from the reaction of SOCl$_2$ with tertiary phosphines or their hydrochlorides, a cyclic transition state is postulated as an intermediate 5 analogous to the one proposed for the oxidation of tertiary phosphines by dimethyl sulfoxide[9b] and by SO$_2$.[9] The over-all mechanism shown in Scheme I is based upon the fact that tertiary phosphines may be readily liberated from their hydrochloride salts by oxygen-free water[1b] and that these weak bases may complex with SOCl$_2$ forming salt-like structures[14] (sulfur dichloride is also capable of exhibiting this behavior[15]). The cyclic transition state 5 forming from the complex 4 is the means by which oxygen is transfered from sulfur to phosphorus. In

this scheme sulfur dichloride is postulated as occurring and the bright yellow coloration of the reaction mixture is support for this assumption. The phosphine oxide formed may be readily chlorinated to the corresponding dichlorophosphorane[12b] by SOCl$_2$ with the elimination of SO$_2$. This is analogous to the splitting out of SO$_2$ in the reaction of sulfoxides with SOCl$_2$.[16]

An entirely similar series of reactions occurs in the chlorination of the hydrochloride of 1. Additionally, however, the alcoholic functions are replaced by halogens. The over-all sequence is presented in Scheme II and accounts for the direct formation of the phosphine oxide 7 when less than 4 moles of SOCl$_2$ are used per mole of 1. In this reaction, it is postulated that the first step involves the formation of trialkyldichlorophosphorane whose structure, according to recent studies,[5a,12b,17] is a quasi-phosphonium one. This salt undergoes an intramolecular cyclization in which the alcoholic function displaces the halogen bound to phosphorus. The replacement of a halogen by an alkoxyl group in the preparation of derivatives of trialkyldichlorophosphoranes in alcoholic solution[18] is support for this type of intramolecular transformation.
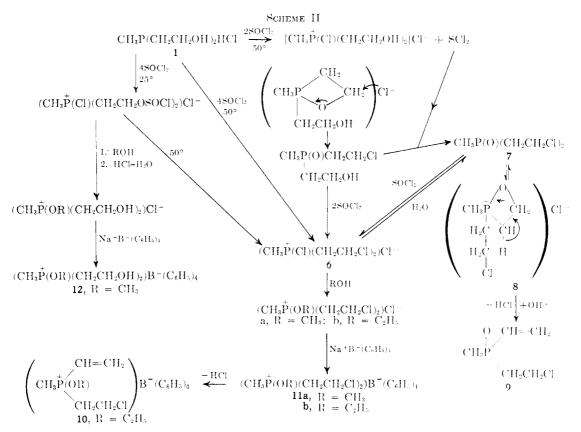
The bis(2-chloroethyl)methyldichlorophosphorane 6 synthesized by various steps in Scheme II is readily hydrolyzed by water to form 7, the phosphorus analog of nitromin. This compound is stable under acidic conditions but undergoes elimination in alkaline solutions. Such a facile liberation of chloride ion may be explained by the neighboring-group participation of the phosphoryl oxygen as shown in Scheme II. The nucleophilic character of the phosphoryl group is well documented[19,20] and a base-initiated ring opening of the oxaphosphetidine (8) could then give the vinylphosphine oxide (9). This compound also appeared to be formed in part in the attempted purification of 7 by vacuum distillation. This is in marked contrast with the reported stability of (2-bromoethyl)dimethyl-

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SCHEME II

$CH_3P(CH_2CH_2OH)_2HCl \xrightarrow[50°]{2SOCl_2} [CH_3\overset{+}{P}(Cl)(CH_2CH_2OH)_2]Cl^- + SCl_2$
1

$CH_3P(CH_2CH_2OSOCl)_2)Cl^-$ (CH_3\overset{+}{P}(Cl)(CH_2CH_2OSOCl)_2)Cl^-

$CH_3P(O)CH_2CH_2Cl$
|
CH_2CH_2OH

$CH_3P(O)(CH_2CH_2Cl)_2$
7

$(CH_3\overset{+}{P}(OR)(CH_2CH_2OH)_2)Cl^-$

$(CH_3\overset{+}{P}(OR)(CH_2CH_2OH)_2)B^-(C_6H_5)_4$
12, R = CH_3

$(CH_3\overset{+}{P}(Cl)(CH_2CH_2Cl)_2)Cl^-$
6

8

$(CH_3\overset{+}{P}(OR)(CH_2CH_2Cl)_2)Cl^-$
a, R = CH_3; b, R = C_2H_5

$O \quad CH=CH_2$
CH_3P
CH_2CH_2Cl
9

$\begin{pmatrix} CH=CH_2 \\ CH_3\overset{+}{P}(OR) \\ CH_2CH_2Cl \end{pmatrix} B^-(C_6H_5)_4 \xleftarrow{-HCl} (CH_3\overset{+}{P}(OR)(CH_2CH_2Cl)_2)B^-(C_6H_5)_4$
10, R = C_2H_5 ; 11a, R = CH_3 ; b, R = C_2H_5

phosphine oxide.[21] Additionally, the phosphonium tetraphenylborate salts containing the 2-chloroethyl group appear to be unstable losing hydrogen chloride on prolonged storage at room temperature or more rapidly at elevated temperatures forming the corresponding vinyl compound (10). Such an elimination reaction normally requires an hydrogen acceptor for initiation.[22,23] Possibly the tetraphenylborate anion acts in this capacity.

Attempts to prepare HP2 by the reduction of the oxide with trichlorosilane[24] were unsuccessful.[25] However, to synthesize a phosphorus analog closer to HN2 in its chemical and biological properties, bis(2-benzoxyethyl)methylphosphine (III) has now been prepared.

Biological Results.—As one means of assessing the "mustard-like" activity of these phosphorus compounds, their effect upon the bone marrow elements in white Swiss Albino mice[26] was determined. In contrast with the results observed[26] with HN2, doses of 7 as high as 1000 mg/kg produced no significant deleterious effects on bone marrow. This result is not surprising in view of the failures to reduce the oxide to the parent phosphine by chemical means. Consequently biological reduction of such a compound would not be expected, in contrast to its nitrogen counterpart. Doses higher

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(25) The ir spectrum of the product still showed a strong phosphoryl absorption, and an elemental analysis showed a loss of chlorine. This could be due to the presence in 7 of a site other than the phosphorus being available for hydride ion transfer from the silicon (L. Herner and W. D. Balzer, Tetrahedron Letters, 1157 (1965)), namely the potentially positive β-carbon atom. Somewhat analogous transfers, from phosphorus to carbon, have recently been postulated for conversion of the group XCPH (X = halogen) by a nucleophile (B) to HCPB (H. Goldwhite and D. G. Rowsell, J. Am. Chem. Soc., 88, 3572 (1966)).

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than 1000 mg/kg were lethal within 2 hr after injection.

It has been reported that trialkyldihalogenophosphoranes and trialkylphosphine oxides do inhibit the growth of Ehrlich ascites mouse carcinoma.[27] In addition, the observed formation of a vinyl-substituted phosphine oxide from 7 (Scheme II) indicates that potential alkylating characteristics are still present (cf. vinyl sulfones[28]). On this basis, 7 was tested for activity against a transplanted murine ependymoblastoma. This test system has been used for the evaluation of clinically useful alkylating agents.[29] In comparison with the growth of untreated controls, 7 at a level of 1000 mg/kg ip showed a slight inhibitory effect on the sixth day following injection. However, subsequently, the growth pattern reverted to that of the untreated animals.

Bis(2-benzoxyethyl)methylphosphine (3) also exhibited no "mustard-like" effect on bone marrow after intraperitoneal doses as great as 300 mg/kg. Intravenous injections of 50 mg/kg and higher produced violent convulsions prior to death. Failure of such compounds to act as alkylating agents even at these levels would appear to support the contention that trialkylphosphines are readily oxidized under in vivo conditions to their corresponding oxides, the latter being devoid of appreciable alkylating activity.

Experimental Section[30]

Bis(2-chloroethyl)methyldichlorophosphorane (6).—To a color-

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less, stirred suspension of 1 (37.7 g, 0.22 mol) in CH_2Cl_2 (300 ml) at $-10°$, $SOCl_2$ (51.8 g, 0.44 mol) in CH_2Cl_2 (100 ml) was added dropwise over 1 hr. A pale yellow emulsion resulted and the stirred reaction mixture was first allowed to attain room temperature (1 hr) and then was gently refluxed for 4 hr. The resultant clear yellow solution was filtered to remove a small amount of colloidal S and concentrated at 20° (10 mm) to a pale yellow syrup (42.0 g) with an ir spectrum identical with bis(2-chloroethyl)methylphosphine oxide (7). This weight corresponds to a quantitative conversion to 7. To a $CHCl_3$ solution (300 ml) of this syrup (34.9, 0.18 mol) at $-10°$ was added dropwise with stirring over a 1-hr period $SOCl_2$ (48.7 g, 0.41 mol) in $CHCl_3$ (120 ml). The mixture was heated to 42° for 2.5 hr. The pale brown solution was concentrated at 20° (10 mm) to give 6 as a highly labile white flocculent solid (26.0 g, 57%), mp 110–112° (sealed tube). This same product was formed in 71% yield by the reaction of 1 (0.18 mol) with $SOCl_2$ (0.73 mol) in $CHCl_3$ at 50°; nmr ($CDCl_3$), δ 4.03 (m, 8.2, CH_2CH_2Cl), 3.07 ppm (d, 2.8, $J = 14$ Hz, CH_3P). Anal. Calcd for $C_5H_{11}Cl_4P$: C, 24.60; H, 4.56; Cl, 58.14; P, 12.70. Found: C, 24.62; H, 4.68; Cl, 55.00, 52.70, 49.90, 48.10; P, 12.80. The results of the analysis for chlorine were variable and consistently low. The highest value was obtained on a freshly prepared sample and subsequent values from aged specimens. The reason may be ascribed to the extreme instability of the phosphorane when exposed to the atmosphere.

Bis(2-chloroethyl)methylmethoxyphosphonium Tetraphenylborate (11a).—The dropwise addition of a methanolic solution of sodium tetraphenylborate (3.26 g, 0.0095 mol) to 6 (2.0 g, 0.0082 mol) in MeOH resulted in the immediate precipitation of 11a (1.0 g, 23%). The product was recrystallized from MeOH to give white prisms of 11a: mp 134–135°; ir (Nujol), 1065, 1060 cm^{-1} (POCH$_3$). Anal. Calcd for $C_{30}H_{34}BCl_2OP$: C, 68.80; H, 6.56; B, 2.08; Cl, 13.55; P, 5.94. Found: C, 68.66; H, 6.55; B, 2.10; Cl, 13.50; P, 5.91.

Repeated attempts at recrystallization resulted in dark brown oils as the only products. Decomposition was also effected by warming the solid at 60° overnight. The use of EtOH as the solvent for the reaction of 6 with sodium tetraphenylborate yielded **bis(2-chloroethyl)methylethoxyphosphonium tetraphenylborate (11b)** as a microcrystalline solid: mp 128.5–129.5°; ir (Nujol), 1045, 1020 cm^{-1} (POC$_2$H$_5$). Anal. Calcd for $C_{31}H_{36}$-BCl$_2$OP: C, 69.33; H, 6.76; B, 2.02; Cl, 13.20; P, 5.79. Found: C, 69.42; H, 6.80; B, 2.14; Cl, 12.50; P, 5.41. The low value found for the per cent chlorine may be due at least in part to the instability of 11b and its conversion, by heating at 60° overnight, to **2-chloroethylmethylethoxyvinylphosphonium tetraphenylborate (10):** mp 133–136°; ir (Nujol), 1600 cm^{-1} (CH=CH$_2$). Anal. Calcd for $C_{31}H_{33}BClOP$: C, 74.33; H, 7.04; B, 21.16; Cl, 7.09. Found: C, 73.88; H, 7.08; B, 2.29; Cl, 6.75.

Bis(2-hydroxyethyl)methylmethoxyphosphonium Tetraphenylborate (12).—To a stirred suspension of 1 (17.7 g, 0.10 mol) in 75 ml of $CHCl_3$ at $-10°$ was added dropwise over 1 hr 49.0 g of $SOCl_2$ (0.41 mol) in 50 ml of dry $CHCl_3$. A thick, yellow paste separated from which gas evolution continued over a 2-hr period. The solvent was decanted and the paste was dissolved in MeOH (150 ml). To this solution 25 ml of 3 N HCl was added to ensure the phosphine's existing as the hydrochloride. The mixture was filtered and concentrated at 25° (0.1 mm) to a pale yellow syrup (17.4 g). An aliquot (2.4 g) in 50 ml of MeOH was converted to the tetraphenylborate salt (12) on the addition of sodium tetraphenylborate (3.9 g) in 50 ml of MeOH. The product was recrystallized from MeOH to give white needles: mp 130–131°; ir (Nujol), 1050 cm^{-1} (POCH$_3$). Anal. ($C_{30}H_{36}BO_3P$): C, 74.00; H, 7.47; B, 2.23; P, 6.38. Found: C, 73.81; H, 7.42; B, 2.40; P, 6.94.

Bis(2-chloroethyl)methylphosphine Oxide (7).—To a stirred, ice-cold solution of the phosphorane (6) (18.7 g, 0.077 mol) in 250 ml of $CHCl_3$, oxygen-free H_2O (40 ml, 2.20 mol) was added dropwise over 10 min. HCl was evolved in a vigorous, exothermic reaction. After stirring for 30 min, the pale yellow organic layer was separated from the aqueous phase (see below), filtered, and dried (Na_2SO_4). Removal of the solvent at 25° (0.1 mm) yielded a light brown oil (9.55 g, 66%) which crystallized below 0°. Sublimation at 50–55° (0.1 mm) gave an analytical sample of 7 as colorless, hydroscopic needles; mp 57.5–58.5° (sealed tube); ir (Nujol), 1170 cm^{-1} (P=O); nmr ($CDCl_3$), δ 3.86 (t, 4, $J = 12$ Hz, $P(O)CH_2CH_2Cl$, and $J = 7.5$ Hz, CH_2CH_2Cl),

2.35 (t, 4, $J = 11$ Hz, $P(O)CH_3$). Anal. Calcd for $C_5H_{11}Cl_2OP$): C, 31.77; H, 5.87; Cl, 37.50; P, 16.38. Found: C, 31.92; H, 5.97; Cl, 37.59; P, 16.74.

The aqueous phase contained a mixture of 7 and 2-chloroethylmethylvinylphosphine (9) as shown by analysis, ir, and nmr. This vinyl compound was also formed in the attempted distillation of 7 or in its treatment with base.

Bis(2-benzoxyethyl)methylphosphine (3).—To a stirred suspension of 1 (29.9 g, 0.173 mol) in Et_2O (300 ml) at $-10°$, a 13% aqueous solution of NaOH (10.4 g, 0.26 mol) was added dropwise over a 20-min period. To the stirred, colorless emulsion which formed, BzCl (53.5 g, 0.38 mol) was added dropwise at 0°. The time of addition was 40 min and then the solution was stirred for an additional 90 min. Excess aqueous NaOH (143 g) was added to the pale yellow emulsion and the ether was separated and dried (K_2CO_3). The solution was separated and the solvent was removed under reduced pressure (0.1 mm) at 25° giving 3 as a slightly cloudy, yellow-green syrup (41.4 g, 69%): nmr ($CDCl_3$), δ 8.06 (m, 4, phenyl *ortho* protons), 7.47 (m, 6, phenyl *meta/para* protons), 4.53 (t, 3.9, $J = 9$ Hz, $PCCH$, and $J = 7.5$ Hz, PCH$_2$CH$_2$), 1.99 (t, 4.10, $J = 1.5$ Hz, PCH$_2$CH$_2$), and 1.20 ppm (d, 3, $J = 3.0$ Hz, PCH$_3$).

The phosphine was characterized by a quantitative conversion to its methiodide. Recrystallization (Me$_2$CO) afforded needles, mp 169.5–170.5°. Anal. Calcd for $C_{20}H_{24}IO_4P$: C, 49.37; H, 4.97; I, 26.10; P, 6.38. Found: C, 49.46; H, 5.06; I, 25.88; P, 6.15. The iodide was readily replaced by the tetraphenylborate anion and the product yielded needles from Me$_2$CO–MeOH; mp 153–155°. Anal. Calcd for $C_{44}H_{44}BO_4P$: C, 77.89; H, 6.53; B, 1.59; P, 4.56. Found: C, 78.34; H, 6.64; B, 1.83; P, 4.61.

The phosphine could be converted to its hydrochloride by the passage of dry HCl through a solution of 3 in CH_2Cl_2. Treatment of the hydrochloride with water regenerated the phosphine (as shown by nmr). Hydrolysis of 3 occurred partially by 5% oxygen-free aqueous $NaHCO_3$ at 68° (4 hr), yielding a mixture of benzoic acid, 3, and 2-benzoxyethyl-2-hydroxyethylmethylphosphine. The latter, an oil, was characterized by conversion through the methiodide to the corresponding tetraphenylborate salt, mp 163–165° (prisms from MeOH). Anal. Calcd for $C_{37}H_{40}BO_3P$: C, 77.33; H, 7.02; B, 1.89; P, 5.39. Found: C, 77.36; H, 7.55; B, 1.90; P, 5.63.

Tri-n-butylphosphonium Tetraphenylborate.—Dry HCl was bubbled through a solution of tri-n-butylphosphine (5.0 g, 0.025 mol) in 80 ml of $CHCl_3$ at 0° for 15 min. Evacuation at 25° (0.1 mm) afforded a hygroscopic viscous syrup (6.8 g, corresponding to the dihydrochloride). Reaction with sodium tetraphenylborate in MeOH yielded the phosphonium salt (67%) which gave needles from MeOH, mp 114° sharp. Anal. Calcd for $C_{36}H_{48}$-BP): C, 82.74; H, 9.25; P, 5.94. Found: C, 82.57; H, 9.33; P, 5.53.

Tri-n-butylmethoxyphosphonium Tetraphenylborate.—$SOCl_2$ (17.9 g, 0.15 mol) in $CHCl_3$ (100 ml) was added to tri-n-butylphosphine (10.1 g, 0.05 mol) in $CHCl_3$ (160 ml) at 0° over a 65-min period. The pale yellow, cloudy solution was heated to reflux for 3 hr, cooled, and filtered. Yellow crystals separated from solution upon concentration at 35° (15 mm). Addition of $CHCl_3$ and reevacuation was repeated twice more and the resulting solid was then washed with dry hexane. The product, tri-n-butyldichlorophosphorane (12b) (13.5 g, 100%), was a highly labile white solid, mp 133–135° (sealed tube). This compound reacted with sodium tetraphenylborate in MeOH to yield the phosphonium salt (33%) which was recrystallized from MeOH to give white needles: mp 133° sharp; ir (Nujol), 1068, 1055 cm^{-1} (POCH$_3$). Anal. Calcd for $C_{37}H_{50}BOP$: C, 80.39; H, 9.14; B, 1.97; P, 5.60. Found: C, 80.24; H, 9.20; B, 2.26; P, 5.66.