O,O,S-Trialkyl Phosphorodithioates were prepared as previously described.[2,3]

General procedure for the aqueous saponification of O,O,S-trialkyl phosphorodithioates. The *O,O,S*-trialkyl phosphorodithioate, 0.5 mole, was added rapidly to a 30% aqueous solution of sodium hydroxide, 2 moles, and heated under reflux for 10 hr. The reaction mixture was cooled to 30°, blown with carbon dioxide for 1 hr. and then steam distilled. The distillate was saturated with sodium chloride and extracted with benzene. The benzene layer was dried over magnesium sulfate. The magnesium sulfate was removed by filtration and the benzene distilled. The products were fractionated under reduced pressure.

Mercaptans were identified by elemental analysis, and the corresponding 2,4-dinitrophenyl alkyl sulfides[4,5] were prepared in order to confirm the structure of the products.

Sulfides were identified by elemental analysis and converted to the sulfones in order to confirm structures.

The esters saponified by this procedure and the products obtained are summarized in Table II.

General procedure for the ethanolic saponification of O,O,S-trialkyl phosphorodithioates. The *O,O,S*-trialkyl phosphorodithioate, 0.4 mole, was added rapidly to a solution of potassium hydroxide, 147 g. (2.6 moles) in 534 g. of 70% ethanol, and heated under reflux for 5 hr. The reaction solution was cooled to 30°, blown with carbon dioxide for 1 hr., and then steam distilled. The isolation and identification procedure used for the products was the same as in the aqueous saponification. The results are summarized in Table III.

General procedure for the glycolic saponification of O,O,S-trialkyl phosphorodithioates. The *O,O,S*-trialkyl phosphorodithioate, 0.5 mole, was added dropwise, to a 34% solution of potassium hydroxide, 0.9 mole, in ethylene glycol, at 140°. The reaction was exothermic and the temperature rose to 160° during the 1-hr. addition period. The products were collected as they distilled from the reaction mixture. The mixture of mercaptan and sulfide was dried over calcium chloride; the calcium chloride was removed by filtration and the products were separated by fractionation at atmospheric pressure. The products were identified by the methods outlined previously. The results of these experiments are shown in Table IV.

Infrared spectra of the esters were measured on the Perkin-Elmer Infracord, Model 137, as neat films on sodium chloride plates.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Phosphorus Compounds. II. Synthesis of Unsymmetrical Tertiary Phosphines[1,2]

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The reduction of benzyl-containing phosphonium compounds with lithium aluminum hydride has been used for the synthesis of two unsymmetrical tertiary phosphines. Thus ethylmethylphenylphosphine was prepared from dichlorophenylphosphine in an over-all yield of 59%. Similarly, ethylmethylpentylphosphine was prepared from dichloromethylphosphine in an over-all yield of 50%.

The methods available for the synthesis of unsymmetrical tertiary phosphines are long and tedious and in general result in poor yields. Kosolapoff[5] lists very few unsymmetrical tertiary phosphines and only one of these contains three aliphatic radicals. The most widely used method for their synthesis, introduced by Hofmann[6] and Michaelis,[7] was one in which the halogens of a phosphorus halide are replaced stepwise by treatment with Grignard reagents, organozinc compounds or organolithium compounds.[8] Although there are new procedures available for the preparation of the monosubstituted dichlorophosphines in good yields,[9-13] the synthesis of disubstituted monochlorophosphines is still somewhat unsatisfactory.[14,15]

The treatment of a phosphine with an alkyl halide appears to be a general synthetic procedure but gives satisfactory yields of an unsymmetrical tertiary phosphine only with unsymmetrical secondary phosphines.[6] Although there are new procedures available for the preparation of primary

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(1) Previous paper in this series, *J. Am. Chem. Soc.*, **79**, 3567 (1957).

(2) This work was done in fulfillment of a contract with the Army Chemical Corps.

(3) Member of the Armed Forces assigned to the Army Chemical Corps, 1954–1956.

(4) Chemical Corps Postdoctoral Fellow, 1957–1959.

(5) G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley and Sons, New York, N. Y., 1950, p. 37.

(6) A. W. Hofmann, *Ber.*, **6**, 292 (1873).

(7) A. Michaelis, *Ann.*, **315**, 53 (1901).

(8) W. C. Davies and F. G. Mann, *J. Chem. Soc.*, 276 (1944).

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(12) T. Weil, B. Prijs and H. Erlenmeyer, *Helv. Chim. Acta*, **35**, 1412 (1955); **36**, 1314 (1956).

(13) R. B. Fox, *J. Am. Chem. Soc.*, **72**, 4147 (1950).

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phosphines,[16,17] a general synthesis of secondary phosphines is not available.

A third method for the preparation of unsymmetrical phosphines, the pyrolysis of quaternary phosphonium halides, usually gives mixtures of products.[18,19]

The previous article in this series[1] reported the facile reduction of benzylphosphonium compounds with lithium aluminum hydride. It was likely, as only one benzyl group was removed at a time, that this reaction could be conveniently adapted to the synthesis of unsymmetrical tertiary phosphines. This method appeared to be attractive, not only because it gave high yields, but also because the starting material could be either phosphorus trichloride or a readily available monosubstituted dichlorophosphine. For these reasons the syntheses of two unsymmetrical tertiary phosphines were undertaken, one completely aliphatic and the other containing an aromatic ring.

The commercially available dichlorophenylphosphine was treated with an excess of benzylmagnesium chloride to produce dibenzylphenylphosphine, which was not isolated but was treated directly with methyl iodide to give an 82% over-all yield of dibenzylmethylphenylphosphonium iodide (I). The iodide I was reduced with a large excess of lithium aluminum hydride in tetrahydrofuran to give the corresponding phosphine, which was treated directly with ethyl iodide to give an 80% over-all yield of benzylethylmethylphenylphosphonium iodide (II). Reduction of II with lithium aluminum hydride gave the desired ethylmethylphenylphosphine (III) in a 90% yield. The phosphine III was characterized by conversion to the solid dimethylethylphenylphosphonium iodide (IV) in a 94% yield. The phosphine III was quite stable to air oxidation. It could be exposed to air with little or no change and air bubbled through a refluxing benzene solution of III produced only slow oxidation.

When dichloromethylphosphine was treated with benzylmagnesium chloride, the resulting dibenzylmethylphosphine was not isolated but was converted directly to the dibenzylethylmethylphosphonium iodide (V) in an 84% over-all yield by treatment with ethyl iodide. Reduction of V with lithium aluminum hydride, followed by treatment of the resulting phosphine with *n*-pentyl iodide, gave benzylethylmethylpentylphosphonium iodide (VI) in an 84% over-all yield. Reduction of VI with lithium aluminum hydride gave a 71% yield of the desired ethylmethylpentylphosphine (IX). In contrast to compound III, the aliphatic phosphine IX is extremely sensitive to air oxidation. The lower yield of IX is partially due to the difficulty in handling the phosphine. Even though atmospheric oxygen was carefully excluded, the distillation residue from IX always contained some phosphine oxide XII.

As in some cases it was difficult to remove all oxygen-containing material by simple distillation, treatment with metallic sodium was used. Curiously, addition of sodium produced a solid material and a blue color which faded on exposure to air. Hein, Plust, and Pohlemann[20] reported the formation of blue phosphyles, $R_3P\cdot \rightarrow O{-}Na$ by the treatment of arylphosphine oxides with sodium. Apparently the introduction of a single phenyl group, as in III, markedly lowers the reactivity toward oxygen. On a preparative scale, heating the phosphine IX in air produced an 85% yield of ethylmethylpentylphosphine oxide (XII). The structure of XII was indicated by reduction with lithium aluminum hydride, followed by direct alkylation of the intermediate phosphine with methyl bromide, to give a 52% yield of dimethylethylpentylphosphonium bromide (XI). XI also could be prepared in an 80% yield by direct alkylation of the phosphine IX.

Treatment of IX with methyl iodide similarly produced an 85% yield of the solid dimethylethylpentylphosphonium iodide (VIII), which also could be prepared in an 81% yield by direct reduction of VI with lithium aluminum hydride, followed by alkylation of the intermediate phosphine with methyl iodide.

Although no solid derivative could be prepared from IX with either picric acid or tetracyanoethylene, mercuric chloride formed both a 1:1 and a 1:2 adduct with IX, depending on the ratio of the reactants.

Several by-products were isolated from the preparation of the tertiary phosphines. In both cases toluene was isolated and characterized through its dinitro derivative. Vapor-phase chromatography indicated that a 96% yield of toluene was obtained from the reduction of VI. It can be speculated that the hydride attacks the benzyl carbon atom with the displacement of the phosphine or the addition of a hydride ion to the phosphorus atom with subsequent rearrangement to the products. The latter possibility would be similar to the mechanism proposed for the decomposition of phosphonium hydroxides[21] and halides.[22] The driving force for either mechanism would be the removal of the formal positive charge on the phosphorus atom. In several reductions small quantities of lower boiling secondary phosphines were detected by odor and vapor-phase chromatography. This observation suggests that some reductive method

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(17) N. Kreutzkamp, *Ber.*, **87**, 919 (1954).

(18) J. Meisenheimer, *Ann.*, **449**, 213 (1906).

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(21) G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 2342 (1929).

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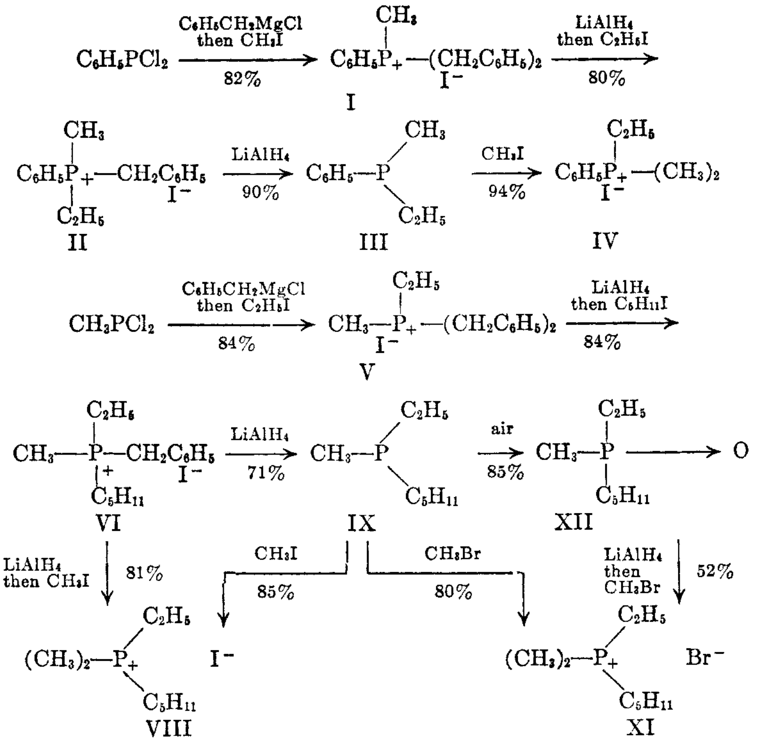

could be used for the synthesis of secondary phosphines. A second by-product isolated from the reductions of II and VI in quite large quantities was *n*-butyl alcohol, which was characterized by conversion to the corresponding 3,5-dinitrobenzoate and by vapor-phase chromatographic analysis. The production of the *n*-butyl alcohol from the tetrahydrofuran will be the subject of a separate report.

The synthesis of ethylmethylphenylphosphine (III) in an over-all yield of 59% and that of ethylmethylpentylphosphine (IX) in an over-all yield of 50% illustrates the versatility and usefulness of this procedure for the preparation of unsymmetrical tertiary phosphines.

EXPERIMENTAL[23]

All phosphines, solutions of phosphines, and Grignard reagents were prepared and handled in an atmosphere of nitrogen purified by passage of the commercial gas through a basic pyrogallol trap, a sulfuric acid trap, and then a tube filled with potassium hydroxide pellets and Drierite.

Dibenzylmethylphenylphosphonium iodide (I). To a solution of benzylmagnesium chloride [prepared in the usual way from 35.7 g. (1.47 g.-atoms) of magnesium, 184.0 g. (1.47 moles) of benzyl chloride, and 1300 ml. of anhydrous ether] cooled in an ice bath was added a solution of 125.5 g. (0.7 mole) of dichlorophenylphosphine (Eastman Kodak Company, technical grade) in 250 ml. of anhydrous ether with stirring and cooling over a period of 4 hr. After the mixture had been heated under reflux for 1 hr. and then allowed to stand for 15 hr., it was hydrolyzed by the cautious addition of 300 ml. of water and 250 ml. of a 20% ammonium chloride solution. The ether layer was separated, dried, and then treated with 200 g. (1.47 moles) of methyl iodide. After the solution was allowed to stand in a tightly stoppered flask for 48 hr., the crystalline solid which formed was removed by filtration and dried to give 266 g. (88%) of slightly impure iodide I, m.p. 201–205°. Recrystallization from a 3:1 mixture of ethanol and ethyl acetate gave 246 g. (82%) of pure dibenzylmethylphenylphosphonium iodide (I), m.p. 207–208° (reported[24] m.p. 206°).

Benzylethylmethylphenylphosphonium iodide (II). To a suspension of 108.0 g. (0.25 mole) of finely powdered dibenzylmethylphenylphosphonium iodide (I) in 900 ml. of dry tetrahydrofuran was added 9.5 g. (0.25 mole) of lithium aluminum hydride. After the mixture was heated under reflux for 30 hr., most of the tetrahydrofuran (750 ml.) was removed by distillation, and 950 ml. of a 20% sodium potassium tartrate solution was added cautiously with cooling in an ice bath. This mixture was then extracted with two 800-ml. portions of ether and the combined dry ether extracts were treated with 117 g. (0.75 mole) of ethyl iodide. After the solution was allowed to stand in a tightly stoppered flask for 9 days, the crystalline solid which deposited was collected, washed with ether, and air dried to obtain 74.0 g. (80%) of crude benzylethylmethylphenylphosphonium iodide (II), m.p. 164–166°. Recrystallization from water gave pure II, m.p. 165–166° (reported[24] m.p. 167–168°). When similar experiments were conducted with smaller quantities of lithium aluminum hydride or for shorter reflux periods, marked reduction in the yield was observed, together with recovery of unchanged starting material.

Ethylmethylphenylphosphine (III). To a suspension of 52.0 g. (0.14 mole) of finely powdered benzylethylmethylphenylphosphonium iodide (II) in 650 ml. of dry tetrahydrofuran was added 5.3 g. (0.14 mole) of lithium aluminum hydride. After the mixture was heated under reflux for 5.5 hr., most of the tetrahydrofuran was removed by distillation and 520 ml. of a 20% sodium potassium tartrate solution was added cautiously. The mixture was then extracted with two 400-ml. portions of ether, and the combined extracts were dried over anhydrous sodium sulfate. After the solvent

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[23] The authors are grateful to Dr. Mary Aldrich, Kathryn Gerdeman, and Jane Swan for the analyses. All melting points and boiling points are uncorrected.

[24] J. Meisenheimer, *Ann.*, **449**, 213 (1926).

was removed by distillation, the residue was fractionated through a 12-inch Vigreux column to yield 15.6 g. of impure toluene, b.p. 45–65° (80 mm.), n_D^{25} 1.4667; 8.9 g. of impure *n*-butyl alcohol, b.p. 65–80° (12–25 mm.), n_D^{25} 1.4012; and 19.1 g. (90%) of slightly impure ethylmethylphenylphosphine (III), b.p. 82–83° (10 mm.), n_D^{25} 1.5522. Redistillation of the tertiary phosphine III gave an analytically pure sample, b.p. 93–94° (14 mm.), n_D^{25} 1.5524, d_{20}^{25} 0.954.

Anal. Calcd. for $C_9H_{13}P$: C, 71.03; H, 8.61. Found: C, 71.20; H, 8.42.

The toluene was further identified by conversion to a solid derivative, 2,4-dinitrotoluene, m.p. 70–71° (reported[25] m.p. 70–71°). A mixed melting point determination with an authentic sample showed no depression. Redistillation of the crude *n*-butyl alcohol at atmospheric pressure gave a fairly pure sample, b.p. 116–117°, n_D^{25} 1.3970 (reported[26] b.p. 117.4°, n_D^{20} 1.3993). A 3,5-dinitrobenzoate, m.p. 64–65° (reported[27] m.p. 64°), was prepared from the *n*-butyl alcohol by the procedure of Shriner and Fuson.[27] A mixed melting point determination with an authentic sample showed no depression.

Dimethylethylphenylphosphonium iodide (IV). To a suspension of 10.0 g. (0.027 mole) of finely powdered benzylethylmethylphenylphosphonium iodide (II) in 125 ml. of dry tetrahydrofuran was added 1.02 g. (0.027 mole) of lithium aluminum hydride. After the mixture was heated under reflux for 5.5 hr., most of the tetrahydrofuran was removed by distillation, and 100 ml. of a 20% sodium potassium tartrate solution was added cautiously. This mixture was then extracted with two 100-ml. portions of ether, and the combined extracts, together with 7.7 g. (0.054 mole) of methyl iodide, were allowed to stand in a tightly stoppered flask for 5 days. The oil which separated was dissolved in methanol, and the solvent was allowed to evaporate slowly to produce 7.46 g. (94%) of crystalline dimethylethylphenylphosphonium iodide (IV), m.p. 144–148°. Recrystallization from isopropyl alcohol gave an analytically pure sample, m.p. 148.5–150° (reported[28] m.p. 137°).

Anal. Calcd. for $C_{10}H_{16}IP$: C, 40.83; H, 5.48. Found: C, 40.57; H, 5.58

Dibenzylethylmethylphosphonium iodide (V). Benzylmagnesium chloride, prepared in the usual way from 37.7 g. (1.55 g.-atoms) of magnesium, 194 g. (1.55 moles) of benzyl chloride and 1350 ml. of anhydrous ether, was cooled in an ice bath, and a solution of 82.0 g. (0.7 mole) of freshly distilled dichloromethylphosphine, b.p. 77–79° (Army Chemical Center, Md.), in 200 ml. of ether was added with stirring and cooling over a period of 4 hr. The mixture was then heated under reflux for 1 hr. and hydrolyzed cautiously with 300 ml. of water and 300 ml. of a 20% ammonium chloride solution. The ether layer was combined with 435 g. (2.8 moles) of ethyl iodide and allowed to stand in a tightly stoppered flask for 14 days. The solution was then filtered to yield 225.5 g. (84%) of impure crystalline dibenzylethylmethylphosphonium iodide (V), m.p. 118–121°. Recrystallization from isopropyl alcohol–ethyl alcohol (3:1) gave an analytically pure sample, m.p. 122.5–123°.

Anal. Calcd. for $C_{17}H_{22}IP$: C, 53.13; H, 5.77. Found: C, 53.41; H, 5.86.

Benzylethylmethylpentylphosphonium iodide (VI). To a suspension of 120 g. (0.312 mole) of finely powdered dibenzylethylmethylphosphonium iodide (V) in 1440 ml. of freshly distilled dry tetrahydrofuran was added 11.85 g. (0.312 mole) of lithium aluminum hydride, and the mixture was heated under reflux for 6 hr. Most of the tetrahydrofuran was then removed by distillation and 1140 ml. of a 20% sodium potassium tartrate solution was added cautiously. This mixture was extracted with four 250-ml. portions of ether, and the combined extracts were dried over magnesium sulfate. After most of the ether was removed by distillation, a solution of 124 g. (0.624 mole) of *n*-pentyl iodide in 100 ml. of freshly distilled *n*-butyl ether was added to the residue. The solution immediately became milky and an oil separated. After the mixture had been heated under reflux for 24 hr., the supernatant liquid was removed by decantation. With cooling, the residual oil crystallized in an hour to yield, on filtration, 95 g. (84%) of crude white benzylethylmethylpentylphosphonium iodide (VI), m.p. 80–82°. Several recrystallizations from isopropyl alcohol–petroleum ether (b.p. 80–100°) gave an analytically pure sample, m.p. 90.5–92.0°.

Anal. Calcd. for $C_{15}H_{26}IP$: C, 49.46; H, 7.19. Found: C, 49.26; H, 7.20.

Benzylethylmethylpentylphosphonium bromide (VII). A suspension of 1.2 g. (0.0031 mole) of dibenzylethylmethylphosphonium iodide (V) in 150 ml. of freshly distilled tetrahydrofuran was reduced with 0.12 g. (0.0032 mole) of lithium aluminum hydride, and the reaction mixture was hydrolyzed as described above. After most of the ether had been removed from the solution containing the benzylethylmethylphosphine, 6.6 g. (0.044 mole) of *n*-pentyl bromide in 15 ml. of methanol was added. This mixture was heated under reflux for 24 hr., and then was allowed to stand for an additional 24 hr. to yield, after removal of the methanol, a semisolid material. Recrystallization from ethyl acetate yielded 0.5 g. (61%) of crude benzylethylmethylpentylphosphonium bromide (VII) in the form of white crystals, m.p. 123–127°. Two further recrystallizations from propanol–ethyl acetate (1:1) gave an analytically pure sample, m.p. 129–130.5°.

Anal. Calcd. for $C_{15}H_{26}BrP$: C, 56.78; H, 8.26. Found: C, 56.84; H, 8.01.

Dimethylethylpentylphosphonium iodide (VIII). *A. From benzylethylmethylpentylphosphonium iodide* (VI). To a suspension of 7.0 g. (0.0192 mole) of finely powdered benzylethylmethylpentylphosphonium iodide (VI) in 75 ml. of dry tetrahydrofuran was added 0.73 g. (0.0192 mole) of lithium aluminum hydride, and the mixture was heated under reflux for 7 hr. After most of the tetrahydrofuran had been removed by distillation, 70 ml. of a 20% sodium potassium tartrate solution was added to the residue. This mixture was extracted with two 80-ml. portions of ether and the combined extracts were treated with 11.4 g. (0.08 mole) of methyl iodide. After this solution was stored in a tightly stoppered flask for 3 days, the oil which formed was separated and dried *in vacuo* to give 4.81 g. of a crude solid. Recrystallization from 8 ml. of methylisobutylcarbinol–ethyl acetate (1:1) gave 4.48 g. (81%) of crystalline dimethylethylpentylphosphonium iodide (VIII), m.p. 106–108°. Two further recrystallizations gave an analytically pure sample, m.p. 108–109°.

Anal. Calcd. for $C_9H_{22}IP$: C, 37.51; H, 7.70. Found: C, 37.29; H, 7.59.

B. From ethylmethylpentylphosphine (IX). To 0.51 g. of ethylmethylpentylphosphine (IX) in 10 ml. of ether was added 1 ml. of methyl iodide in 20 ml. of ether with stirring and cooling with ice-water over a 30-min. period. The solution immediately turned milky and an oil, which solidified within 30 min., separated to give 0.85 g. (85%) of the crude iodide VIII. Recrystallization from propanol–ethyl acetate (1:2) gave fairly pure dimethylethylpentylphosphonium iodide (VIII), m.p. 108–108.5°. A mixed melting point determination with an authentic sample showed no depression.

Ethylmethylpentylphosphine (IX). To a suspension of 69 g. (0.19 mole) of finely powdered benzylethylmethylpentylphosphonium iodide (VI) in 1150 ml. of tetrahydrofuran

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[25] E. A. Huntress and S. P. Mulliken, *Identification of Pure Organic Compounds*, John Wiley and Sons, New York, N. Y., 1941, p. 520.

[26] I. Heilbron, *Dictionary of Organic Compounds*, Oxford University Press, New York, N. Y., 1953, p. 388.

[27] R. L. Shriner and R. C. Fuson, *Identification of Organic Compounds*, 3rd edition, John Wiley and Sons, New York, N. Y., 1949.

[28] A. Michaelis, *Ann.*, **181**, 362 (1876).

(freshly distilled from lithium aluminum hydride) was added 8.9 g. (0.23 mole) of lithium aluminum hydride, and the mixture was heated under reflux for 8 hr. After most of the tetrahydrofuran was removed by distillation over a 12-hr. period, the residue was treated cautiously with 600 ml. of a 25% sodium potassium tartrate solution with cooling and stirring. This mixture was then extracted with three 200-ml. portions of ether, which were removed through a glass tube by the application of an excess of nitrogen pressure. After the combined ether solutions were dried over anhydrous sodium sulfate, the ether and most of the tetrahydrofuran were removed by distillation through an 8-inch, helix-packed column. The residue was fractionated through the same column to give the following fractions:

Fraction	B.P., °	Mm.	Wt., g.	n_D^{25}
1	100–112	755	32.6	1.4489
2	112–114.5	755	7.0	1.4042
3	60–41	60–21	4.3	1.4081
4	68–73.5	21	19.5	1.4551
5	Residue	—	2.9	—

The impure ethylmethylpentylphosphine (IX), contained in fraction 4, was obtained in a 71% yield. Redistillation of fraction 4 through a 5-inch Podbielniak column (which had been alternately evacuated and flushed with nitrogen six times) yielded an analytically pure sample, b.p. 74–74.5° (22 mm.), n_D^{20} 1.4574. (Satisfactory analyses were obtained only if the combustion was carried out at 900°.)

Anal. Calcd. for $C_8H_{19}P$: C, 65.72; H, 13.09. Found: C, 65.53; H, 12.94.

Vapor-phase chromatography indicated that fractions 1 through 3 contained 16.5 g. (96%) of toluene, 20.5 g. of *n*-butyl alcohol, and 6.8 g. of tetrahydrofuran. The toluene was further identified as its 2,4-dinitro derivative, m.p. 70–71°, which did not depress the melting point of an authentic sample. The *n*-butyl alcohol was converted to its 3,5-dinitrobenzoate, m.p. 65.0–65.5°, which did not depress the melting point of an authentic sample.

Ethylmethylpentylphosphine-mercuric chloride addition compounds (X). When 0.4 g. (0.0027 mole) of ethylmethylpentylphosphine (IX) was added to a solution of 0.63 g. (0.0023 mole) of mercuric chloride in 20 ml. of ethanol, no precipitate was formed. Removal of the solvent on a steam bath produced a gray, sticky solid, m.p. 120–205°. Extraction of this solid with ethanol, followed by removal of the ethanol from the extracts on a steam bath, yielded a clear, sticky film, which was redissolved in hot ethanol. When the solution was allowed to cool to room temperature, an oil separated which solidified in the refrigerator. Three recrystallizations from ethanol produced white crystals of a 1:1 adduct of ethylmethylpentylphosphine and mercuric chloride (Xa), m.p. 67.5–68.5°.

Anal. Calcd. for $C_8H_{19}Cl_2HgP$: Cl, 16.97. Found: Cl, 16.77.

Repetition of the procedure described above, but with double the quantity of mercuric chloride, produced a 1:2 adduct of ethylmethylpentylphosphine and mercuric chloride (Xb), m.p. 155–155.5°. With continued heating, the molten Xb resolidified to produce a solid, which was recrystallized from ethanol to produce a pure sample of Xb, m.p. 210°.

Anal. Calcd. for $C_8H_{19}Cl_4Hg_2P$: Cl, 20.57; P, 4.49. Found: Cl, 20.59; P, 4.67.

Stoichiometric quantities of reactants are recommended, as purification of the adducts by recrystallization from ethanol is difficult. However, an excess of mercuric chloride can be conveniently removed by extraction with boiling water in which the adducts are only sparingly soluble.

Dimethylethylpentylphosphonium bromide (XI). To 0.8 g. (0.0054 mole) of ethylmethylpentylphosphine (IX) dissolved in 20 ml. of ether was added 3 ml. of methyl bromide at −15°. After the mixture was allowed to stand for 5 days at room temperature, the ether solution was decanted from an oil which solidified after being dried in a desiccator at 1 mm. pressure to produce 1.25 g. (80%) of very crude hygroscopic dimethylethylpentylphosphonium bromide (XI), m.p. 116–121°. Two recrystallizations from ethyl acetate–propanol (20:1) produced an analytically pure sample, m.p. 128–128.5°.

Anal. Calcd. for $C_9H_{22}BrP$: C, 44.81; H, 9.19. Found: C, 44.51; H, 9.19.

Ethylmethylpentylphosphine oxide (XII). After a mixture of 15 g. of ethylmethylpentylphosphine (IX) and the residue (2.9 g.) from the distillation of IX was heated for 4 hr. in the air, the reaction product was distilled at reduced pressure to yield 17 g. (86%) of crude ethylmethylpentylphosphine oxide (XII). Redistillation through an 8-inch, helix-packed column gave pure XII, b.p. 76–76.5° (0.4 mm.), n_D^{20} 1.4591, m.p. 8–9°, as a colorless, very hygroscopic liquid.

Anal. Calcd. for $C_8H_{19}OP$: C, 59.26; H, 11.81. Found: C, 59.37; H, 11.53.

Reduction of ethylmethylpentylphosphine oxide (XII) *with lithium aluminum hydride.* A solution of 1.14 g. (0.007 mole) of ethylmethylpentylphosphine oxide (XII) in 10 ml. of tetrahydrofuran was added to 0.3 g. of lithium aluminum hydride in 90 ml. of tetrahydrofuran. After the mixture had been heated under reflux for 5 hr., the mixture was worked up in the usual way, as described above. To the combined ether extracts was added 6 g. of methyl bromide, and the mixture was allowed to stand for 5 days at room temperature to yield 0.88 g. (52%) of crude dimethylethylpentylphosphonium bromide (XI), m.p. 110–114°. Three recrystallizations from propanol–ethyl acetate raised the melting point to 127.5–129°. A mixed melting point determination with an authentic sample of XI showed no depression.

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