to a 15-fold excess of diazomethane in ether (110 ml.).[6] The slightly yellow solution was allowed to crystallize at 4° for several hours, filtered, and washed with cold methanol; yield 1.2 g., m.p. 245–247°. Recrystallization from boiling methanol afforded an analytical sample melting sharply at 250°: ν_{max}^{KBr} 2980 (m), 1780 (vs), 1520 (s), 1475 (s), 1365 (m), 1270 (s), 1220 (m), 1050 (m), 990 (s), 870 (m), 770 (s), and 660 cm.$^{-1}$ (m).

Anal. Calcd. for $C_{23}H_{26}O_9S$: C, 57.9; H, 5.49; S, 6.70; OCH_3, 32.4; mol. wt., 478. Found: C, 57.62, 57.45; H, 5.48, 5.52; S, 6.72; OCH_3, 31.41; mol. wt., 476.

Acknowledgment.—The authors wish to thank Crown Zellerbach, Chemical Products Division, Camas, Washington, for their generous sample of α-conidendrin.

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[6] A. I. Vogel, "A Text Book of Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 844.

Cyclodehydrohalogenation of Diarylphosphinous Chlorides[1]

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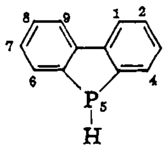
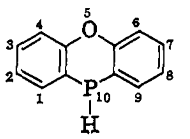
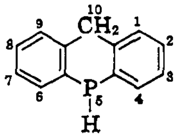
Cyclodehydrohalogenation of arylphosphonous dichlorides has previously been shown to be a useful method for the preparation of certain heterocyclic organophosphorus compounds.[2] By means of this method we have prepared derivatives of dibenzophosphole (I), phenoxaphosphine (II), and 5,10-dihydrodibenz[*b*,*e*]phosphorin (III).



I

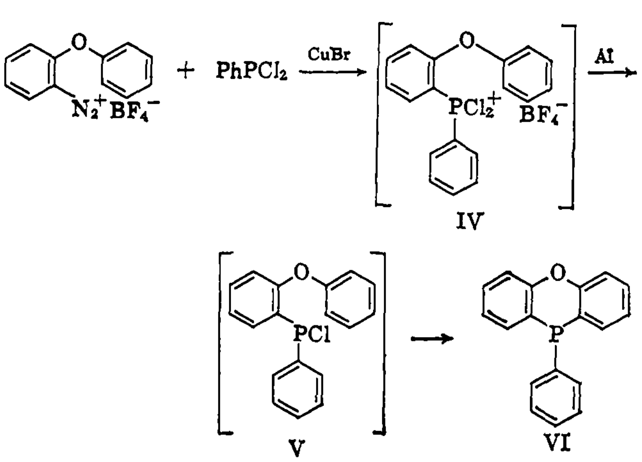


II

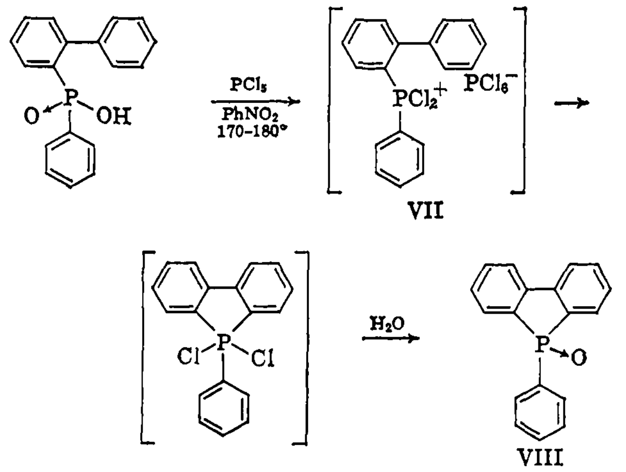


III

We have now found that suitably substituted diarylphosphinous chlorides[3] also undergo cyclodehydrohalogenation. Thus 10-phenylphenoxaphosphine[4] (VI) was prepared in 26% yield by the following series of reactions. Neither IV nor V was isolated from these reactions. (*o*-Phenoxyphenyl)phenylphosphinous chloride (V) presumedly underwent cyclodehydrohalogenation during the preparation and yielded the desired cyclic compound. The intermediate formed from the reaction of a diazonium tetrafluoroborate with an arylphosphonous dichloride has not been isolated, but structures similar to IV have been proposed.[3,5,6]



Campbell and Way have suggested that intermediate VII was formed in their preparation of 5-phenyldibenzophosphole 5-oxide (VIII) from *o*-biphenylylphenylphosphinic acid.[7] Since the structure suggested for IV is similar to that given for VII, we have investigated the possibility that cyclodehydrohalogenation occurs before the aluminum reduction in the preparation of 10-phenylphenoxaphosphine. Accordingly, *o*-phenoxybenzenediazonium tetrafluoroborate was allowed to react with phenylphosphonous dichloride, and the resulting mixture was hydrolyzed. The uncyclized compound, (*o*-phenoxyphenyl)phenylphosphinic acid, was isolated in 52% yield. This result strongly suggests that cyclodehydrohalogenation occurred after the aluminum reduction in our preparation of 10-phenylphenoxaphosphine.



Some cyclization did occur, however, when the reaction mixture was distilled rather than hydrolyzed. Thus, when the highest boiling fraction of the distillate (b.p. 175–177° at about 5 μ) was treated with an alkaline hydrogen peroxide solution (to hydrolyze the mixture and to oxidize any trivalent phosphorus compound which may have been formed from thermal decomposition of a pentavalent phosphorus compound), the resulting mixture gave a 3% yield of 10-phenylphenoxaphosphine 10-oxide and a 32% yield of (*o*-phenoxyphenyl)phenylphosphinic acid. It is of interest to note that we have been unable to cyclize this acid by the method used by Campbell and Way for the cyclization of *o*-biphenylylphenylphosphinic acid.

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[1] Supported by Research Grant GM-09479 from the National Institutes of Health, U. S. Public Health Service.

[2] G. O. Doak, L. D. Freedman, and J. B. Levy, *J. Org. Chem.*, **29**, 2382 (1964).

[3] L. D. Quin and R. E. Montgomery, *ibid.*, **28**, 3315 (1963).

[4] 10-Phenylphenoxaphosphine and its oxide have been prepared by F. G. Mann and I. T. Millar [*J. Chem. Soc.*, 3746 (1953)].

[5] L. D. Quin and J. S. Humphrey, Jr., *J. Am. Chem. Soc.*, **83**, 4124 (1961).

[6] P. C. Crofts, *Quart. Rev.* (London), **12**, 341 (1958).

[7] I. G. M. Campbell and J. K. Way, *J. Chem. Soc.*, 2133 (1961).

The reaction of p-tolylphosphonous dichloride with o-phenoxybenzenediazonium tetrafluoroborate, followed by reduction with powdered aluminum, gave a mixture from which we were able to isolate a 19% yield of p-tolylphenoxaphosphine and, after oxidation and hydrolysis, an 11% yield of (o-phenoxyphenyl)-p-tolylphosphinic acid. We have prepared two additional cyclic tertiary phosphines from o-biphenyldiazonium tetrafluoroborate. 5-Phenyldibenzophosphole[7,8] was prepared in 21% yield, and 5-p-tolyldibenzophosphole was obtained in 7% yield. In the latter reaction a small amount of o-biphenylyl-p-tolylphosphinic acid was also isolated. Oxidation of all four cyclic phosphines with hydrogen peroxide yielded the corresponding phosphine oxides, 10-phenylphenoxaphosphine 10-oxide,[4] 10-p-tolylphenoxaphosphine 10-oxide, 5-phenyldibenzophosphole 5-oxide,[7,8] and 5-p-tolyldibenzophosphole 5-oxide.

Experimental[9-11]

10-Phenylphenoxaphosphine.—o-Phenoxybenzenediazonium tetrafluoroborate (56.8 g., 0.2 mole), 200 ml. of anhydrous ethyl acetate, 35.8 g. of phenylphosphonous dichloride (0.2 mole, Eastman P 6544), and 4 g. of cuprous bromide were allowed to react according to the procedure described for the preparation of 5-chlorodibenzophosphole.[2] After 45 min. of stirring the mixture was heated to initiate the vigorous reaction. Stirring was continued for 1 hr., and 3.6 g. of powdered aluminum (Mallinckrodt) was added to the flask. The mixture was refluxed for 1 hr. and then stirred overnight. The usual isolation procedure was carried out[2]; the product (19.0 g., b.p. 150° at about 5 μ) was collected as a liquid which later solidified. The yield after recrystallization from aqueous alcohol was 14.3 g. (26%), m.p. 97.5–98.0° (lit.[4] m.p. 94.5–95.0°).

Anal. Calcd. for $C_{18}H_{13}OP$: P, 11.21. Found: P, 11.38.

10-Phenylphenoxaphosphine 10-Oxide.—10-Phenylphenoxaphosphine was oxidized in an alkaline solution of aqueous ethanol and hydrogen peroxide. The precipitate which appeared on evaporation of the ethanol was removed by filtration, washed with water, and recrystallized from 6 N hydrochloric acid which contained about 5% ethanol; m.p. 176–179° (lit.[4] m.p. 173–174°). The yield was 94%. An intense absorption at 1205 cm.$^{-1}$ was assigned to the phosphoryl (P→O) bond.

Anal. Calcd. for $C_{18}H_{13}O_2P$: P, 10.60. Found: P, 10.36.

(o-Phenoxyphenyl)phenylphosphinic Acid.—o-Phenoxybenzenediazonium tetrafluoroborate (14.2 g., 0.05 mole), 60 ml. of anhydrous ethyl acetate, and 8.5 g. of phenylphosphonous dichloride (0.05 mole) were allowed to react as in the preparation of 10-phenylphenoxaphosphine. After the diazonium salt was decomposed, stirring was continued for 45 min. The mixture was refluxed for 1 hr. and then filtered through a sintered-glass funnel. Water (50 ml.) was added to the filtrate, and the ethyl acetate was evaporated. After the addition of 150 ml. of 10% sodium hydroxide, the mixture was stirred for 1 hr., acidified with concentrated hydrochloric acid, and extracted with ether. When the ether layer was shaken with 20% sodium hydroxide, a sodium salt precipitated, which was removed by filtration, washed with ether, and then dissolved in water. The material which precipitated upon acidification of the aqueous solution was removed by filtration and recrystallized from aqueous ethanol; m.p. 164–166°. The yield was 8.2 g. (52%).

Anal. Calcd. for $C_{18}H_{15}O_3P$: P, 9.98; neut. equiv., 310.3. Found: P, 9.96; neut. equiv., 311.5.

5-Phenyldibenzophosphole.—The reaction of o-biphenyldiazonium tetrafluoroborate (26.8 g., 0.1 mole) with phenylphosphonous dichloride (0.1 mole), followed by reduction with powdered aluminum, was carried out as described for the preparation of 10-phenylphenoxaphosphine. The usual isolation procedure led to 8.1 g. of 5-phenyldibenzophosphole (b.p. 180° at about 5 μ). The yield after recrystallization from aqueous alcohol was 5.5 g. (21%), m.p. 92–94° (lit. m.p. 90–92°,[7] 93–94°[8]). The infrared absorption spectrum was in agreement with that previously reported.[8]

Anal. Calcd. for $C_{18}H_{13}P$: P, 11.90. Found: P, 12.01.

5-Phenyldibenzophosphole 5-Oxide.—5-Phenyldibenzophosphole was oxidized in an alkaline solution of aqueous ethanol and hydrogen peroxide. After two recrystallizations from 6 N hydrochloric acid which contained about 5% ethanol, the melting point of 5-phenyldibenzophosphole 5-oxide was 165–167° (lit. m.p. 167–168°,[7] 163.5–166.5°[8]); 94% yield. The infrared absorption spectrum was in agreement with that previously reported.[7]

Anal. Calcd. for $C_{18}H_{13}OP$: P, 11.21. Found: P, 11.07.

p-Tolylphosphonous Dichloride.—This compound (b.p. 90° at about 5 μ) was prepared by the method of Quin and Humphrey[5] except that powdered aluminum was used as the reducing agent rather than magnesium. The yield was 28.5%.

10-p-Tolylphenoxaphosphine and (o-Phenoxyphenyl)-p-tolylphosphinic Acid.—The reaction of o-phenoxybenzenediazonium tetrafluoroborate (28.4 g., 0.1 mole) with p-tolylphosphonous dichloride and reduction with powdered aluminum were carried out as described for the preparation of 10-phenylphenoxaphosphine. A liquid (10.3 g., b.p. 180° at about 5 μ) was collected and dissolved in ethanol. Deaerated water was added to the solution to precipitate 5.5 g. (19% yield) of 10-p-tolylphenoxaphosphine, m.p. 53–57°. The melting point of the phosphine after recrystallization from aqueous ethanol was 59–62°.

Anal. Calcd. for $C_{19}H_{15}OP$: P, 10.67. Found: P, 10.41.

The original mother liquor from 10-p-tolylphenoxaphosphine was oxidized with hydrogen peroxide. The solution was made alkaline, stirred with Norit, and filtered. Upon acidification, (o-phenoxyphenyl)-p-tolylphosphinic acid (3.6 g., 11% yield) precipitated. After two recrystallizations from aqueous ethanol, the melting point was 174–177°.

Anal. Calcd. for $C_{19}H_{17}O_3P$: P, 9.55; neut. equiv., 324.3. Found: P, 9.36; neut. equiv., 334.0.

10-p-Tolylphenoxaphosphine 10-Oxide.—10-p-Tolylphenoxaphosphine was oxidized in an alkaline solution of aqueous ethanol and hydrogen peroxide. After recrystallization from 6 N hydrochloric acid (which contained about 5% ethanol) the melting point of 10-p-tolylphenoxaphosphine 10-oxide was 195–197°; 95% yield. An intense absorption at 1200 cm.$^{-1}$ was assigned to the phosphoryl (P→O) bond.

Anal. Calcd. for $C_{19}H_{15}O_2P$: P, 10.11. Found: P, 9.97.

5-p-Tolyldibenzophosphole and o-Biphenylyl-p-tolylphosphinic Acid.—The reaction of o-biphenyldiazonium tetrafluoroborate (26.8 g., 0.1 mole) with p-tolylphosphonous dichloride and reduction with powdered aluminum were carried out as described for the preparation of 10-phenylphenoxaphosphine. A liquid (3.2 g., b.p. 180° at about 5 μ) was collected and dissolved in ethanol. Deaerated water was added to the solution to precipitate 1.9 g. (7% yield) of 5-p-tolyldibenzophosphole. The melting point of the phosphine after recrystallization from aqueous ethanol was 110–113°.

Anal. Calcd. for $C_{19}H_{15}P$: P, 11.29. Found: P, 11.18.

The original mother liquor from 5-p-tolyldibenzophosphole was oxidized with hydrogen peroxide. The solution was made alkaline, stirred with Norit, and filtered. Upon acidification, o-biphenylyl-p-tolylphosphinic acid (0.2 g.) precipitated. The melting point after recrystallization from aqueous ethanol was 179–180°.

Anal. Calcd. for $C_{19}H_{17}O_2P$: P, 10.05; neut. equiv., 308.3. Found: P, 9.91; neut. equiv., 311.6.

5-p-Tolyldibenzophosphole 5-Oxide.—5-p-Tolyldibenzophosphole was oxidized in an alkaline solution of aqueous ethanol and hydrogen peroxide. The melting point of 5-p-tolyldibenzophosphole 5-oxide, after recrystallization from aqueous ethanol, was 190–192°; 94% yield. An intense absorption at 1200 cm.$^{-1}$ was assigned to the phosphoryl (P→O) bond.

Anal. Calcd. for $C_{19}H_{15}OP$: P, 10.67. Found: P, 10.66.

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(8) G. Wittig and G. Geissler, *Ann.*, **580**, 44 (1953).

(9) The infrared spectra were taken on a Perkin-Elmer Model 521 spectrophotometer. The samples were run in potassium bromide pellets.

(10) Melting points were determined on a Fisher-Johns apparatus with a thermometer calibrated against U.S.P. reference standards as previously described; *cf.* G. O. Doak and L. D. Freedman, *J. Am. Chem. Soc.*, **73**, 5658 (1951).

(11) Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.