2-Aminophenyl 5-chloro-2-nitrophenyl sulfide (IV). To a solution of 38.4 g. (0.20 mole) of 2,4-dichloronitrobenzene and 25.2 g. (0.20 mole) of 2-aminobenzenethiol in 670 ml. of isopropyl alcohol was added dropwise, with stirring, a solution of 13.2 g. of 85% potassium hydroxide in 30 ml. of 95% ethanol. The mixture was then refluxed for 3 hr. After refluxing, a bright orange precipitate was present in the mixture.

The mixture was then evaporated, under vacuum, to dryness; the residual solid was washed well with water and air-dried. The crude product melted from 124–132°. Recrystallization from absolute ethanol gave 43.8 g. (78%) of orange crystals, melting at 132–133.5°. This material was employed in the subsequent experiment without further purification. An analytical sample of the 2-aminophenyl 5-chloro-2-nitrophenyl sulfide melting at 135–136° was obtained by an additional recrystallization from absolute ethanol.

Anal. Calcd. for $C_{12}H_9ClN_2O_2S$: Cl, 12.63; N, 9.98; S, 11.42. Found: Cl, 12.57; N, 9.93; S, 11.52.

2-Acetamidophenyl 5-chloro-2-nitrophenyl sulfide (V). A mixture of 16.3 g. (0.058 mole) of the above sulfide, 110 ml. of acetic anhydride, 7 ml. of pyridine, and 2 g. of charcoal was heated for 2 hr. on a steam bath and filtered hot. The pale yellow filtrate was concentrated to dryness, leaving 17.4 g. (93%) of a bright yellow solid. The material melted from 143–150° and was found suitable for the next experiment without further purification.

Recrystallization of a portion of the crude 2-acetamidophenyl 5-chloro-2-nitrophenyl sulfide, first from benzene and then from absolute ethanol, gave an analytical sample as pale yellow needles, m.p. 154.4–155°.

Anal. Calcd. for $C_{14}H_{11}ClN_2O_3S$: Cl, 10.99; N, 8.68; S, 9.93. Found: Cl, 10.80; N, 8.77; S, 9.91.

2-Chlorophenothiazine (I). To 888 ml. of acetone was added a solution of 6.8 g. of 85% potassium hydroxide in 51 ml. of 95% ethanol. After this mixture had been stirred and diffused with nitrogen for 15 min., 16.1 g. (0.05 mole) of the crude acetamido derivative was added and the solution was refluxed for 3 hr. Approximately 600 ml. of the acetone was removed by distillation under a nitrogen atmosphere; 500 ml. of petroleum ether (b.p. 90–120°), and 700 ml. of water were then added to the residual liquid. A small amount of insoluble material present was removed by filtration. After separation of the two layers, the aqueous layer was washed with an additional 200 ml. of petroleum ether and the organic layer was washed with 200 ml. of water. The combined petroleum ether solutions were dried over magnesium sulfate and reduced in volume to 60 ml. by distillation. Cooling, filtering, and washing the resulting precipitate with cold petroleum ether (b.p. 20–40°) gave 5.5 g. of a brown solid which melted from 180–193°, with prior shrinkage. This material was recrystallized (Norit) from xylene to give 4.3 g. (37%) of pale yellow crystals melting at 194.5–196.5°. An additional recrystallization from xylene gave 3.6 g. of almost colorless crystals, m.p. 196–197°. A mixture melting point with an authentic sample[15] of 2-chlorophenothiazine showed no depression; also, the infrared spectra[16] of the two specimens were identical.

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OHIO UNIVERSITY
ATHENS, OHIO

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Tris(o-methoxymethylphenyl)phosphine

R. L. LETSINGER, J. R. NAZY,[1] AND A. S. HUSSEY

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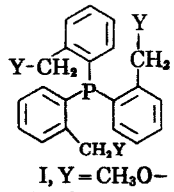
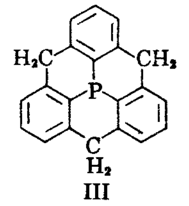
The intramolecular alkylation of the phosphine I or II would lead to the formation of III, an interesting new type of arylphosphine.



I, Y = CH_3O–
II, Y = Cl



III

While electrophilic substitution in the aromatic rings of triphenylphosphine is difficult, the nitration of triphenylphosphine to tris(*m*-nitrophenyl)phosphine oxide has been accomplished.[2] Further, the intramolecular alkylation of I would involve a reaction-assisting six-membered cyclic transition state. Accordingly, we have examined the effect of acids on phosphine I, using reagents ranging from formic acid, sulfuric acid in acetic acid, liquid hydrogen fluoride, stannic chloride, and aluminum chloride to concentrated sulfuric acid. All attempts to effect cyclization of I to III, however, have been unsuccessful. Some tris(*o*-methoxymethylphenyl)-phosphine oxide was recovered from a run employing aluminum chloride in nitromethane. Unreacted I and intractable tars were the only materials isolated from the other reactions.

Phosphine I was prepared by the reaction of *o*-lithiobenzyl methyl ether with phosphorus trichloride, the lithium reagent having been obtained by interchange between *n*-butyllithium and *o*-bromobenzyl methyl ether.[3] The phosphine reacted normally with hydrogen peroxide and with iodine to give the phosphine oxide, and with methyl iodide to give the methylphosphonium iodide.

Cleavage of the ether functions with boron trichloride[4] furnished tris(*o*-chloromethylphenyl)phosphine, II. Eighty-five percent of II was recovered unchanged from a reaction in liquid hydrogen fluoride. Aluminum chloride in nitromethane, however, converted II to tris(*o*-chloromethylphenyl)phosphine oxide (87%).[5] There was no indication that III was formed in either case.

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[1] National Science Foundation Fellow.

[2] F. Challenger and J. Wilkinson, *J. Chem. Soc.*, 125, 2675 (1924).

[3] The corresponding Grignard reagent has been described by F. Holliman and F. G. Mann, *J. Chem. Soc.*, 1634 (1947).

[4] W. Gerrard and M. F. Lappert, *J. Chem. Soc.*, 1486 (1952).

[5] The oxidizing agent may have been air. Triphenylphosphine is oxidized in air in the presence of aluminum chloride to triphenylphosphine oxide; D. R. Lyon and F. G. Mann, *J. Chem. Soc.*, 666 (1942).

EXPERIMENTAL

Tris(o-methoxymethylphenyl)phosphine, I. Butyllithium (850 cc. of 0.86*M* solution; 0.73 mole) was dropped (2.5 hr.) into a cold (−75°), efficiently stirred solution of *o*-bromobenzyl methyl ether[5] (141 g., 0.701 mole) in 300 cc. of dry ether under nitrogen. (Carbonation with Dry Ice of a similar reaction mixture permitted the isolation of 62% of *o*-methoxymethylbenzoic acid, m.p. 89–92°, showing that the interchange had proceeded as desired. Recrystallization from hexane raised the melting point to 95–95.5°.)[6] The addition of 32 g. (0.233 mole) of phosphorus trichloride in 100 cc. of ether over a period of 15 min., warming to room temperature, followed by stirring for 20 hr. and 1 hr. at reflux converted the lithio derivative to the phosphine I. The reaction mixture was hydrolyzed by addition, with supplemental cooling, of 350 cc. of saturated aqueous ammonium chloride. Concentration of combined ether extracts furnished large, colorless crystals of the phosphine; 43.7 g., m.p. 105–106°. Another 8.8 g. of phosphine was collected on further evaporation of the solvent; total yield, 58%. Distillation of the liquid residue yielded 35.7 g. (38%) of *n*-butyl bromide.

An analytical sample was prepared by recrystallization of the phosphine from 95% ethanol; m.p. 105.5–106°.

Anal.[7] Calcd. for $C_{24}H_{27}O_3P$: C, 73.08; H, 6.90. Found: C, 72.79; H, 6.91.

Tris(o-methoxymethylphenyl)phosphine oxide. (*a*) Oxidation with Iodine. To a solution of 0.82 g. of phosphine I in 15 cc. of ether was added 0.6 g. of iodine in 30 cc. of ethanol and six drops of pyridine. In contrast to the reaction of triphenylphosphine with iodine, which decolorizes immediately, the iodine color in this preparation slowly faded during 20 min. heating on a steam bath. Excess iodine was reduced by a few drops of sodium bisulfite solution, then 10 cc. of water was added to the chilled solution. The precipitate was washed twice with water and dried; 0.70 g. (81%) of crude oxide; m.p. 146.5–147.5°. Two recrystallizations from alcohol raised the melting point to 147–147.5°; weight 0.49 g. (57%).

Anal.[7] Calcd. for $C_{24}H_{27}O_4P$: C, 70.23; H, 6.63. Found: C, 69.87; H, 6.71.

(*b*) Hydrogen peroxide. Hydrogen peroxide (0.3 g. of 30% solution) with a few cubic centimeters of water was added to a solution of 0.90 g. of phosphine I in 20 cc. of acetone. Most of the acetone was removed *in vacuo*, leaving 0.92 g. (97%) of the phosphine oxide; m.p. 145–146°; 146–147° after recrystallization. It did not depress the melting point of the oxide prepared by iodine oxidation.

Methyl tris(o-methoxymethylphenyl)phosphonium iodide. A mixture consisting of 1.42 g. of the phosphine I, 16.3 g. of methyl iodide, and 0.5 g. of fine copper wire was refluxed on a steam bath for 1 hr.; then excess methyl iodide was distilled. Removal of the copper left 1.93 g. (99%) of white crystals; m.p. 202–202.5°. Reactions carried out in the absence of copper developed a yellow color which was difficult to remove from the crystalline product. Two recrystallizations of the methiodide from ethanol gave 1.55 g. (80%) of product with a slightly higher melting point; 202.5–203°.

Anal.[7] Calcd. for $C_{25}H_{30}O_3PI$: C, 55.98; H, 5.64. Found: C, 56.29; H, 5.53.

Tris(o-chloromethylphenyl)phosphine, II. To 11.5 g. (0.098 mole) of boron trichloride in an ice cooled flask was slowly added 8.90 g. (0.0226 mole) of phosphine I. The mixture was kept cold for 8 hr., then 40 cc. of pentane was added and the mixture allowed to warm to room temperature overnight. The caked solid was washed with water, heated to remove pentane, and washed again with water. On drying 7.5 g. of solid, m.p. 117–131°, was obtained. Recrystallization from ethanol-water gave 4.03 g. of material melting at 132–137°. Subsequent recrystallizations from alcohol and from chloroform raised the melting point to 140–141°.

Anal.[7] Calcd. for $C_{21}H_{18}Cl_3P$: C, 61.86; H, 4.45. Found: C, 62.02; H, 4.33.

This phosphine was converted to its oxide in 94% yield with 30% hydrogen peroxide by the procedure described above; m.p. 178–181°. Recrystallization two times from chloroform-pentane gave the pure oxide, m.p. 185–185.5°, which exhibited the characteristic strong absorption in the infrared at 8.45μ attributed to P—O bonding.[8,9]

Anal.[7] Calcd. for $C_{21}H_{18}Cl_3OP$: C, 59.52; H, 4.28. Found: C, 59.56: H, 4.33.

Reaction of II with aluminum chloride. (*a*) Nitromethane solvent. The chloromethylphenylphosphine II, (0.42 g.) in 15 cc. of nitromethane was added to a solution of 0.55 g. of aluminum chloride in 20 cc. of nitromethane and the mixture was heated on a steam bath for 40 hr. The mixture was poured into dilute hydrochloric acid and nitromethane was removed by steam distillation. On cooling, a brown solid (0.38 g., 87%) was recovered, m.p. 172–175°. Its infrared spectrum was the same as that of the phosphine oxide, IV.

(*b*) Aluminum chloride. To 1.1 g. of aluminum chloride in 15 cc. of carbon disulfide was slowly added 0.75 g. of II in 15 cc. of carbon disulfide. The solution immediately turned a deep red. After standing at room temperature for 2 hr. it was poured onto ice, hydrochloric acid was added, and the organic layer was separated and washed with water, dried, and warmed to distill the carbon disulfide. Crystals (0.40 g., 53%) of phosphine II, as shown by the infrared spectrum, remained. Recrystallization from ether-pentane yielded 0.30 g. of recovered phosphine, m.p. 135–137°. Some tars insoluble in ether or concentrated hydrochloric acid were also obtained from the reaction mixture.

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NORTHWESTERN UNIVERSITY
EVANSTON, ILL.

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(7) Carbon and hydrogen analyses by Miss H. Beck.

(8) L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

(9) Our infrared spectra were taken in a Baird double beam recording spectrophotometer. The sample was dispersed in a plate of potassium bromide.

2-Nitro-9,10-ψ-dinitrosophenanthrene[1]

J. H. BOYER AND G. MAMIKUNIAN

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Symmetry requirements for *o*-dinitroso aromatic compounds, *e.g.* 4-methyl-1,2-ψ-dinitrosobenzene (I), do not allow the structural assignment as isomeric furoxanes, *e.g.* 5-(6-) methylbenzfuroxane (II), although they have been so described since 1912.[2,3] Meisenheimer, Lange, and Lamparter demonstrated the unsymmetrical nature of the furoxane ring in a preparation of isomeric furoxanes by an oxidation of corresponding γ-(*amphi*)

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(1) Partial support of this work under contract DA-01-009-ORD-428 with the Office of Ordnance Research is gratefully acknowledged.

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(3) J. H. Boyer, R. F. Reinisch, M. J. Danzig, G. A. Stoner, and F. Sahhar, *J. Am. Chem. Soc.*, **77**, 5688 (1955).