the second case. The raw nmr data is assembled in two tables. Table III records proton signals for the hydrocarbons in cycles per second relative to the internal reference. Table IV records the signals for the nitro derivatives.

Chlorosulfonation of Triphenyl Phosphate, Diphenyl Methylphosphonate, and Triphenylphosphine Oxide

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Reports of substitution reactions on aryl groups either attached directly to phosphorus or through carbon as in tertiary phosphine oxides are quite meager. The majority of such reactions have been confined to nitration of the aryl substituent.[1] Stachlewska–Wroblowa and Okon[2] have, in addition to nitration, investigated the sulfonation and chlorosulfonation of triphenylphosphine oxide and its derivatives. The chlorosulfonation of 4-methoxyphenylphosphonic acid to yield 3-chlorosulfonyl-4-methoxyphenylphosphonic acid was also reported in a patent.[3]

Of particular interest to us was the chlorosulfonation of triphenylphosphine oxide and the possible extension of the chlorosulfonation reaction to neutral pentavalent phosphorus esters containing at least one aryl group. The subject of electrophilic substitution reactions involving such phosphorus esters has received even less attention than that afforded tertiary phosphine oxides. In both cases substitution on the pendant aryl group is most often effected prior to formation of the phosphorus ester or phosphine oxide. This is usually desirable especially in the case of the somewhat labile phosphorus esters. In view of this lability, the stability of aryloxy phosphorus bonds, particularly toward chlorosulfonic acid and the attending conditions, was somewhat questionable.

Subsequently, it was found that triphenyl phosphate can be chlorosulfonated readily with apparently little deleterious effect on the aryloxy phosphorus bond. Addition of the phosphate to excess chlorosulfonic acid at room temperature caused a readily controlled exotherm, and hydrogen chloride was evolved. Moderate heating of the reaction mixture, until hydrogen chloride evolution subsided, followed by conventional work-up, yielded chlorosulfonated triphenyl phosphate. The reaction product was identified by elemental analysis, molecular weight determination, and infrared and pmr spectra as tris(p-chlorosulfonylphenyl) phosphate (1). The reaction conditions were not opti-

mized. However, variation of the molar ratio of reactants, while maintaining reaction time and temperature constant, indicated that a 30:1 mole ratio of chlorosulfonic acid to phosphate reacted at 50° for 6 hr afforded high yields (>80%) of crude 1. The reaction was repeated several times using these conditions with comparable results. When chlorosulfonic acid and triphenyl phosphate were allowed to react at molar ratios of 24:1, 18:1, and 12:1, the yields of crude chlorosulfonated phosphate (1) were 77, 73, and 54%, respectively. Reported[4] methods for reducing the amount of excess chlorosulfonic acid, such as the utilization of sodium chloride, alone or in combination with inert organic solvents (e.g., carbon tetrachloride), were not investigated.

The chlorosulfonation of diphenyl methylphosphonate was also found to proceed readily, utilizing reaction conditions that produced high yields of chlorosulfonated triphenyl phosphate (1) and a mole ratio of chlorosulfonic acid to phosphonate of 20:1. The reaction product identified as bis(p-chlorosulfonylphenyl) methylphosphonate (2) by elemental analysis, molecular weight determination, and infrared and pmr spectra was obtained in better than 79% crude yield.

That chlorosulfonation of triphenyl phosphate and diphenyl methylphosphonate occurs predominately at the *para* position was demonstrated by the infrared and pmr spectra of the reaction products. *para* substitution of both the chlorosulfonated phosphate (1) and phosphonate (2) was manifested by characteristic infrared absorption in the regions 6.3–7.2 μ and 11.5–12.5 μ. The pmr spectrum of 1 in $CDCl_3$ (TMS as internal reference) exhibited the characteristic AB quartet of a *para*-substituted benzene (τ_A 1.82, τ_B 2.42 ppm; J_{AB} = 8.7 cps). The chlorosulfonated

$$\tau_B\ 2.42 \qquad \tau_A\ 1.82$$
1

$$\tau_B\ 2.51 \qquad \tau_A\ 1.90$$
2
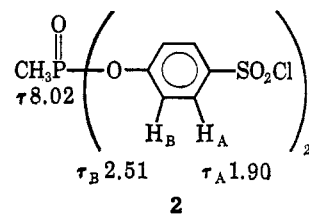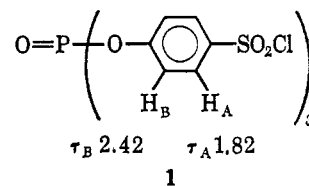
phosphonate (2) in $CDCl_3$ showed the expected methyl doublet (τ = 8.02 ppm,[2] J_{PH} = *ca.* 18 cps) for P–CH$_3$ and the characteristic AB pattern of a *para*-substituted benzene (τ_A = 1.90, τ_B = 2.51 ppm; J_{AB} = 8.7 cps). In both 1 and 2, a long-range coupling of phosphorus to H$_B$ ($^4J_{PH}$ = 1.0 cps) was observed and provided further support for the assigned structures. Similar four-bond couplings have been observed in a number of other organophosphorus compounds.[5] In neither case was there any evidence for the presence of other isomers in amounts greater than *ca.* 5%. In the case of the

(1) K. D. Berlin and G. B. Butler, *Chem. Rev.*, **60**, 243 (1960).

(2) (a) A. Stachlewska-Wroblowa and K. Okon, *Biul. Wojskowej Akad. Tech.*, **10**, No. 4, 3 (1961); *Chem. Abstr.*, **56**, 14322d (1962); (b) A. Stachlewska-Wroblowa and K. Okon, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, **9**, 281 (1961).

(3) E. M. Hardy, U. S. Patent 3,017,321 (1962).

(4) E. E. Gilbert, "Sulfonation and Related Reactions," Interscience Publishers, Inc., New York, N. Y., 1965, p 84.

(5) (a) M. Gordon, Ph.D. Thesis, University of Pittsburgh, 1965; (b) C. E. Griffin, R. B. Davison, and M. Gordon, *Tetrahedron*, **22**, 561 (1966).

chlorosulfonated phosphate 1 the crude reaction product, melting over a rather broad range (115–119°) after one recrystallization, gave a pmr spectrum comparable to that of analytically pure material.

In addition to the spectral evidence for *para* substitution, basic hydrolysis of the chlorosulfonated phosphate (1) gave 1-phenol-4-sulfonic acid in 48% yield. The sulfonic acid was identified as its S-benzylthiuronium salt by melting point and mixture melting point with an authentic sample.

In the case of tris(*p*-chlorosulfonylphenyl) phosphate (1), an alternate synthesis was briefly considered, involving reaction of phosphorus pentachloride or phosphorus oxychloride with 1-phenol-4-sulfonic acid. This route was abandoned in view of the reported[6] initial formation of *p*-chlorosulfonylphenyl phosphorodichloridate and desulfonation under more forceful conditions.

The chlorosulfonation of triphenylphosphine oxide was investigated in order to confirm earlier reports.[2] Repetition of the reported procedure gave negligible amounts of the desired chlorosulfonated triphenylphosphine oxide. Use of longer reaction times and a larger excess of chlorosulfonic acid than reported[2] resulted in improved yields (Table I) of the chlorosulfonated triphenylphosphine oxide.

TABLE I

EFFECT OF REACTION TIME AND MOLE RATIO OF REACTANTS
ON THE YIELD OF CHLOROSULFONATED
TRIPHENYLPHOSPHINE OXIDE (3)[a]

Run no.	ClSO₃H:Ph₃PO mole ratio	Reaction time, hr	Yield of 3, %[c]
Lit.[2]	12:1	3	30
1[b]	12:1	3	. . .
2	25:1	3.5	24(13)
3	25:1	20	78(58)

[a] Reaction temperature 130°. [b] Repeat of reported procedure.[2] [c] Yield of purified reaction product (3) in parenthesis.

Identification of the reaction product as tris(*m*-chlorosulfonylphenyl)phosphine oxide (3) was made by elemental analysis and infrared and pmr spectra.

The pmr spectrum of 3 in DMSO-d_6 gave a pattern in the aromatic region that is characteristic of *meta* substitution; the multiplet structure was quite similar to that observed in tetramethyl *m*-phenylenediphosphonate and dimethyl *m*-carboxyphenylphosphonate. The chemical shifts and coupling constants for the individual aromatic protons could not be determined by inspection due to the complexity of the spectrum. It was estimated that less than 10% of other isomers was present.

3
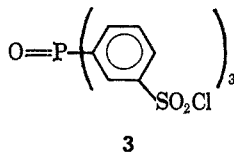
In none of the chlorosulfonation reactions investigated were reaction products isolated bearing more than a single sulfonyl chloride group per phenyl ring of the organophosphorus moiety. In addition, the results indicated that the phenyl esters of phosphoric

(6) C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p 459.

and phosphonic acids undergo a more facile chlorosulfonation than do tertiary phosphine oxides bearing at least one phenyl group attached directly to phosphorus. Since the phosphoryl group of the phosphine oxide is electron withdrawing and, therefore, deactivating to electrophilic substitution, more forceful chlorosulfonating conditions are required than for either the phosphate or phosphonate.

Starting Materials.—Triphenyl phosphate practical grade (Eastman Organic Chemicals) was recrystallized from 95% ethyl alcohol (168 g/100 ml of solvent). Material melting at 48–50° (lit.[8] mp 50°) was used in our work. Diphenyl methylphosphonate, bp 137–139° (0.05 mm), n^{20}D 1.5533 [lit.[9] bp 151° (0.8 mm)], was prepared in 54% yield according to the procedure of Morgan and Herr.[9] Triphenylphosphine oxide, mp 155.5–157° (lit.[10] mp 156–157°), was obtained in 83% yield by allowing the corresponding phosphine (Metal and Thermit Co.) to react with hydrogen peroxide. Chlorosulfonic acid, practical grade, (Eastman Organic Chemicals), was distilled; the fraction, bp 149–156° (752.8 mm), was retained.

Chlorosulfonation of Triphenyl Phosphate.—Triphenyl phosphate (195.8 g, 0.6 mole) was added in 20 min under a positive nitrogen pressure to stirred, chlorosulfonic acid (2093 g, 18 moles) maintained at 22–24° by means of a cold-water bath. The phosphate dissolved immediately and hydrogen chloride was evolved. Upon completing the addition, the clear, pale yellow reaction mixture was heated to 50 ± 1° and maintained at these temperatures for 6 hr. The cooled, clear, pale amber reaction mixture when carefully added dropwise to a suitable quantity of crushed ice caused a white solid to precipitate. The white precipitate was filtered and pressed dry; the slightly yellow clear acidic aqueous filtrate was discarded. Chloroform (2900 ml) was added to the filter cake causing most of the solid to dissolve. Chloroform insolubles, a small quantity of gelatinous semisolid and an equally small aqueous phase, were extracted with portions of fresh solvent. The combined chloroform extracts were washed consecutively with two 50-ml portions of aqueous 10% sodium bicarbonate and three 100-ml portions of aqueous saturated sodium chloride, and dried over anhydrous magnesium sulfate.

Concentration of the dried chloroform layer to *ca.* 500 ml gave a white, solid slurry that upon dilution with 500 ml of hexane and cooling gave a white solid. The filtered and dried crude tris(*p*-chlorosulfonylphenyl) phosphate (1), 304.4 g, 82%,) softened at 103° and melted at 110–118°. Recrystallization of the crude reaction product 1 from 3000 ml of a 3:1 (v/v) carbon tetrachloride–benzene solution gave 265.3 g of a white solid, mp 115–119°.

An analytical sample (mp 119–121°) was prepared by repeated recrystallization from a benzene–hexane mixture. The recrystallized product 1 was very soluble in acetonitrile, dioxane, methyl ethyl ketone, methylene chloride, and diglyme. Infrared absorption (KBr) occurred at 6.32 (s), 6.74 (s), 7.1 (m), 7.26 (s), 7.61 (s), 7.73 (m), 8.0 (m), 8.32 (s), 8.45 (s), 8.60 (s), 9.25 (m), 10.16 (s), 10.42 (s), 10.67 (m), and 11.85 (s) μ. *Anal.* Calcd for C₁₈H₁₂Cl₃O₁₀PS₃ (1): C, 34.77; H, 1.95; Cl, 17.11; P, 4.98; S, 15.47; mol wt, 621.83. Found: C, 34.96; H, 1.96; Cl, 17.19; P, 4.99; S, 15.70: mol wt, 593.3 (determined in THF by vapor phase osmometry).

Hydrolysis of Tris(*p*-chlorosulfonylphenyl) Phosphate (1).—A stirred mixture of alcoholic potassium hydroxide (25.8 g, 0.46 mole of base in 400 ml of 95% ethyl alcohol) and 18.6 g (0.03 mole) of 1 was refluxed for 15 hr in a stainless steel reactor. Neutralization of the cooled hydrolysate with concentrated hydrochloric acid (14 ml) precipitated a cream-colored solid. The filtered precipitate washed consecutively with alcohol and ether left 34.03 g (after drying) of an insoluble solid.

(7) Melting and boiling points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville 21, Tenn. Infrared absorption spectra were obtained with a Perkin-Elmer Infracord Model 137B spectrophotometer. Pmr spectra were determined with a Varian Associates A-60 spectrometer.

(8) S. Sugden, J. Reed, and H. Wilkins, *J. Chem. Soc.*, **127**, 1525 (1925).

(9) P. Morgan and B. Herr, *J. Am. Chem. Soc.*, **74**, 4526 (1952).

(10) R. J. Kennedy and A. M. Stock, *J. Org. Chem.*, **25**, 1901 (1960).

S-Benzylthiuronium chloride (5.06 g, 0.02 mole) was allowed to react with a portion (3.92 g) of the insoluble solid dissolved in water to precipitate a solid (4.61 g). After one recrystallization from hot water, the crude product (1.1 g) was identified as the S-benzylthiuronium salt of 1-phenol-4-sulfonic acid by melting point and mixture melting point with the authentic salt (lit.[11] mp 168.7°).

Chlorosulfonation of Diphenyl Methylphosphonate.—The procedure described for the chlorosulfonation of triphenyl phosphate was repeated using 63.3 g (0.26 mole) of diphenyl methylphosphonate and 602 g (5.16 moles) of chlorosulfonic acid. Addition of the reaction mixture to ice, extraction with chloroform, and concentration of the combined, washed, and dried chloroform extracts followed by dilution of the concentrate (250 ml) with pentane precipitated an oil. The solvent layer was decanted and the oil on trituration with fresh ice-cold pentane solidified. The filtered, washed, and dried white solid (78.3 g) melted at 81–86°. A second crop of product (13.6 g), melting at 85–87.5°, was obtained upon dilution of the chloroform–pentane filtrate with the nonsolvent pentane. The combined fractions (91.9 g) of crude bis(p-chlorosulfonylphenyl) methylphosphonate (2) melted at 83–86°.

Two recrystallizations of the crude reaction product 2 from a 50:50 benzene–ligroine mixture raised the melting point to 84.5–87°. Infrared absorptions (KBr) appeared at 3.23 (w), 6.33 (s), 6.76 (s), 7.07 (m), 7.28 (s), 7.55 (m), 7.73 (m), 7.85 (m), 8.04 (s), 8.26 (s), 8.45 (s), 8.59 (s), 9.24 (w), 10.50 (m), 10.81 (s), 11.81 (m), 11.96 (m), and 13.45 (s) μ. *Anal.* Calcd for $C_{13}H_{11}Cl_2O_7PS_2$ (2): C, 35.07; H, 2.49; Cl, 15.92; P, 6.95; S, 14.40; mol wt, 445.24. Found: C, 35.08; H, 2.60; Cl, 15.82; P, 7.02; S, 14.45; mol wt, 457.0 (determined cryoscopically in benzene).

Chlorosulfonation of Triphenylphosphine Oxide.—Excess chlorosulfonic acid (289 g, 2.48 moles) was added dropwise to triphenylphosphine oxide (27.8 g, 0.1 mole) with stirring and cooling. Upon completing the addition, the reaction mixture was heated to 130°. The reaction temperature was maintained for *ca.* 20 hr. The cooled reaction mixture was added dropwise to crushed ice and a solid precipitated. The filtered solid was washed consecutively with water, ethyl alcohol, and ether. After drying *in vacuo* at 45°, the crude reaction product (44.6 g) was recrystallized from a chloroform–hexane mixture to give 33 g (57.5%) of tris(m-chlorosulfonylphenyl)phosphine oxide (3), mp 217–221° (lit.[2] mp 210–212°). Repeated recrystallization from chloroform–hexane raised the melting point to 220–225°. The product 3 showed infrared absorption (KBr) at 3.2 (w), 6.3 (w), 6.4 (w), 6.83 (w), 7.09 (s), 7.24 (s), 7.65 (w), 7.86 (w), 8.37 (s), 8.47 (s), 8.82 (s), 9.24 (m), 10.08 (w), 12.31 (s), 12.44 (s), and 14.66 (s) μ. *Anal.* Calcd for $C_{18}H_{12}Cl_3O_7PS_3$ (3): C, 37.67; H, 2.11; Cl, 18.54; P, 5.40; S, 16.76. Found: C, 37.20; H, 2.40; Cl, 18.34; P, 5.22; S, 16.41.

(11) N. Cheronis and J. Entrikin, "Semi-micro Qualitative Organic Analysis," Interscience Publishers, Inc., New York, N. Y., 1958, p 697.

Chloromethylphosphine[1]

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It has recently been suggested that α-fluoroalkylphosphines undergo reactions with nucleophiles by an elimination–addition reaction sequence.[2,3] To test the generality of this reaction pattern for compounds containing the grouping CX–PH (X = halogen) the previously unknown chloromethylphosphine has been prepared and its reactions with some nucleophiles have been examined.

The preparation of primary phosphines by the thermal decomposition of phosphinic acids has found its widest application in the aromatic series. The yields of primary aliphatic phosphines from the corresponding phosphinic acids are generally low.[4] The production of primary phosphines can be represented by the following disproportionation. The other product is an alkylphosphonic acid.

$$3RPO_2H_2 \xrightarrow{\Delta} RPH_2 + 2RP(O)(OH)_2$$

Chloromethylphosphinic acid, synthesized from chloromethylphosphonic dichloride by the method of Uhing, Rattenbury, and Toy[5] decomposed violently, *even explosively,* when heated *in vacuo.* However, if the reaction was carried out by allowing the acid to drop slowly into an evacuated flask heated to 150–160°, a steady evolution of a mixture of hydrogen chloride and chloromethylphosphine was obtained. The chloromethylphosphine was separated from hydrogen chloride by washing with water. The yield of chloromethylphosphine was somewhat variable and, at best, was only about 35%.

The gas-phase infrared spectrum of chloromethylphosphine (see the Experimental Section) contained bands attributable to CH, PH, and CCl stretching modes. The proton magnetic resonance spectrum of neat chloromethylphosphine consisted of a complex multiplet attributed to the $ClCH_2$ group ($\delta_{ClCH_2} = 3.78$ ppm (downfield from internal $(CH_3)_4Si$)), and two widely separated multiplets attributed to the PH_2 group ($\delta_{PH} = 3.40$ ppm and $J_{HP} = 206$ cps). The area ratios agreed with this interpretation. The four protons of chloromethylphosphine probably constitute an A_2B_2 system which is further complicated by coupling of all four protons to phosphorus. A full analysis of this spectrum is in progress.

The reaction between chloromethylphosphine and aqueous sodium hydroxide solution gave hydrogen as the only volatile product. The other reaction product was methylphosphinic acid $CH_3P(O)(H)(OH)$. The identity of this product was suggested by its proton magnetic resonance spectrum, which consisted of four equal peaks attributed to CH_3P ($J_{HCP} = 15.3$ cps; $J_{HCPH} = 2.0$ cps) and two widely spaced quartets attributed to PH ($J_{PH} = 530$ cps). Fiat, *et al.,*[6] reported the following values for aqueous solutions of methylphosphinic acid: CH_3P ($J_{HCP} = 15.7$ cps; $J_{HCPH} = 2.15$ cps) and PH ($J_{PH} = 561$ cps). Oxidation of the phosphinic acid gave methylphosphonic acids, $CH_3P(O)(OH)_2$; the proton magnetic resonance spectrum of the aqueous solution of this compound was identical with that of a sample prepared by the alkaline hydrolysis of chloromethyl phosphinic acid.[5]

(1) This investigation was supported by Public Health Service Research Grant CA 07182 from the National Cancer Institute.
(2) G. M. Burch, H. Goldwhite, and R. N. Haszeldine, *J. Chem. Soc.,* 572 (1964).
(3) H. Goldwhite, R. N. Haszeldine, and D. G. Rowsell, *ibid.,* 6875 (1965).
(4) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p 12.
(5) E. Uhing, K. Rattenbury, and A. D. F. Toy, *J. Am. Chem. Soc.,* **83,** 2299 (1961).
(6) D. Fiat, M. Halmann, L. Kuzel, and J. Reuben, *J. Chem. Soc.,* 3837 (1962).