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.

Acknowledgment.—The author wishes to thank Mr. W. E. Byrne for the pmr spectra and their interpretation and Messrs. W. Whitmore and D. Hershey for carrying out some of the experiments.

[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 (δ_{ClCH_2} = 3.78 ppm (downfield from internal $(CH_3)_4Si$)), and two widely separated multiplets attributed to the PH_2 group (δ_{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]

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[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).

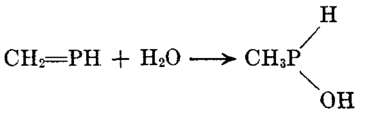
An elimination–addition mechanism has been suggested in order to account for the reactions of primary and secondary polyfluoroalkylphosphines with nucleophilic reagents.[2,3] A similar type of mechanism is one possibility for the alkaline hydrolysis of chloromethylphosphine. The first step could be the removal of a proton attached to phosphorus. Loss of chloride

$$CH_2ClPH_2 + \bar{O}H \longrightarrow CH_2Cl\bar{P}H + H_2O$$

ion could then give a phosphaalkene intermediate.

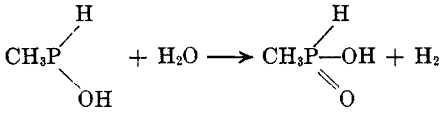
$$CH_2Cl\bar{P}H \longrightarrow CH_2{=}PH + Cl^-$$

Addition of water across the phosphorus–carbon double bond would give an unstable acid. The production of



$$CH_2{=}PH + H_2O \longrightarrow CH_3P(H)(OH)$$

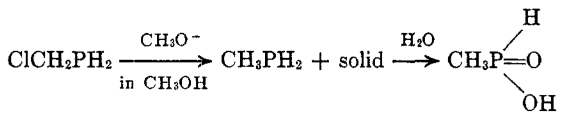
hydrogen and methylphosphinic acid can be represented by the following equation. A number of phosphorus



$$CH_3P(H)(OH) + H_2O \longrightarrow CH_3P(H)({=}O){-}OH + H_2$$

acids containing P–H bonds are known to react with aqueous sodium hydroxide solution to produce hydrogen,[7] but the mechanisms involved have not been investigated in detail.

The reaction between chloromethylphosphine and sodium methoxide in methanol solution gave methylphosphine accounting for approximately 40% of the phosphorus. The other reaction product was an apparently polymeric involatile material which could not be dissolved without decomposition; hydrolysis of this material gave only methylphosphinic acid. Methylphosphine (31%) was again obtained as the only volatile product when chloromethylphosphine was treated with trimethylamine; an involatile polymeric material which also gave only methylphosphinic acid on hydrolysis was the other product.



$$ClCH_2PH_2 \xrightarrow[\text{in } CH_3OH]{CH_3O^-} CH_3PH_2 + \text{solid} \xrightarrow{H_2O} CH_3P(H)({=}O)(OH)$$

It is difficult to suggest adequate mechanisms for these reactions, especially since the nature of the involatile solid precluded establishment of its structure. However, it is significant that in both reactions the eventual fate of the $ClCH_2P$ group was conversion into a CH_3P group, and some type of elimination–addition process would certainly account for this.

Experimental Section

Materials.—Chloromethylphosphonic acid was prepared from chloromethylphosphonic dichloride by the published procedure.[5]

Spectra.—The proton magnetic resonance spectra were determined on a Varian A-60 spectrometer at ambient probe temperature.

The infrared spectrum of chloromethylphosphine in the gas phase was determined on a Beckman IR-12 spectrometer; the following bands (frequencies given in cm^{-1}; sh = shoulder) were observed and tentatively assigned as follows: 2960, 2955, 2950 (CH str); 2328, 2314, 2300, 2290, 2283 (PH str); 1420, 1411, 1405 (CH def); 1232, 1216, 1208, (sh), 1202 (sh); 1090, 1079, 1075 (sh); 943, 940, 935; 883, 878, 872, 854, 847, 843, 839; 764, 760, 750 (CCl str); 630 (sh), 611, 596 (sh).

Molecular weights were determined by measurement of gas densities.

Preparation of Chloromethylphosphine.—A 250-ml, three-necked flask was connected to a conventional vacuum system and evacuated. The flask was heated to 150–160° and chloromethylphosphinic acid (20.0 g, 175 mmoles) was slowly added *via* a dropping funnel. When the acid came in contact with the heated flask a smooth evolution of gas occurred. The volatile products passed into the vacuum system and were condensed in a trap cooled to −196°. When the addition of acid was complete, the contents of the −196° trap were subjected to vacuum fractionation. Hydrogen chloride (1.90 g, 52 mmoles) condensed at −196° and chloromethylphosphine, containing some hydrogen chloride, condensed at −80°. The −80° fraction was condensed into a 50-ml bulb containing water (10 ml). The bulb was allowed to attain room temperature and was shaken. The water-insoluble volatile fraction was taken into the vacuum system, fractionated, dried by condensing onto phosphoric oxide, and finally refractionated to give chloromethylphosphine (1.50 g, 18.2 mmoles, 31%) condensing at −65°, bp (isoteniscope) 68°. *Anal.* Calcd for CH_2ClPH_2: Cl, 43.0; mol wt, 82.5. Found: Cl, 43.7; mol wt, 83.0.

Reaction between Chloromethylphosphine and Aqueous Sodium Hydroxide Solution.—Chloromethylphosphine (0.17 g, 2.0 mmoles) was condensed into a 100-ml bulb containing sodium hydroxide (1.0 g, 25 mmoles) in water (10 ml). The mixture was allowed to attain room temperature. The evolution of noncondensable gas was complete in approximately 30 min. The gas was removed using a Sprengel pump and was identified by combustion over copper oxide as hydrogen (1.4 mmoles). The ^1H nmr spectrum of the aqueous residue showed only four peaks of equal height centered at δ_{CH_3P} = 1.37 ppm, with J_{HCP} = 15.3 cps, and J_{HCPH} = 2.0 cps, and two quartets centered at δ_{PH} = 7.40 ppm, with J_{PH} = 530 cps and J_{HCPH} = 2.0 cps. This solution was refluxed with an excess of hydrogen peroxide for 2 hr. The ^1H nmr of the reaction mixture then consisted solely of a doublet at δ = 1.20 ppm with J_{HP} = 17.0 cps.

A solution of sodium methylphosphonate was prepared by the reaction between chloromethylphosphinic acid and aqueous sodium hydroxide solution.[5] The ^1H nmr of the solution was identical with that of the product obtained above, showing that the oxidation product was methylphosphonic acid (lit.[5] J_{HCP} = 17.3 cps for methylphosphonic acid).

Reaction between Chloromethylphosphine and Sodium Methoxide.—Chloromethylphosphine (0.50 g, 6.0 mmoles) was condensed into a 50-ml bulb containing a solution of sodium methoxide (0.72 g, 13.3 mmoles) in methanol (10 ml). The bulb was kept at −80° for 15 min during which time a white precipitate was slowly produced. The mixture was kept at room temperature for 1 hr. The volatile products were taken into the vacuum system and fractionated. The −80° fraction was identified by infrared spectroscopy as methanol. The −196° fraction was shown by infrared and nmr spectroscopy to be methylphosphine (0.11 g, 2.3 mmoles). *Anal.* Calcd for CH_3PH_2: mol wt, 48.0. Found: mol wt, 49.0. The solid residue in the reaction vessel was dissolved in water (5 ml). The nmr spectrum of the solution confirmed the presence of methylphosphinic acid; no other species containing phosphorus bound to an organic group was detected. It is estimated that this method would have detected such compounds if they were present in an amount not less than 10% of the methylphosphinic acid present.

Reaction between Chloromethylphosphine and Trimethylamine.—Chloromethylphosphine (0.53 g, 6.4 mmoles) and trimethylamine (0.81 g, 13.8 mmoles) were condensed into a glass reaction tube (50-ml capacity). The tube was allowed to attain room temperature. After 1 hr the volatile products were taken into the vacuum system and fractionated. The volatile fraction condensed at −196° and was shown by nuclear magnetic resonance spectroscopy to be a mixture of trimethylamine (0.53 g, 8.9 mmoles) and methylphosphine (0.10 g, 2.0 mmoles). The solid residue was dissolved in water; nmr spectroscopy of the solution indicated that methylphosphinic acid was the sole species containing an organic group bound to phosphorus present.

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[7] J. VanWazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1958, p 363.

Acknowledgment.—We thank Victor Division of the Stauffer Chemical Company for generous gifts of chloromethylphosphonic dichloride.

Reactions of Triphenylsilyl Azide with Tetraphenyldiphosphine and Diphenylphosphine

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Triphenylsilyl azide reacts readily with triphenylphosphine to give the phosphinimine.[2,3] With chlorophosphines exchange of the azido and chloro groups occurs concurrently with nitrogen evolution resulting in the formation of phosphonitriles and quantitative recovery of the alkyl- or arylsilyl moiety in the form of the chloride.[4] The reaction of phosphine with phenyl azide investigated by Staudinger and Hauser[5] is the only case in which the behavior of a P–H bond during the interaction with an azide could be studied. Although the authors seem to have failed in the isolation of a pure material, they point out that the initial reaction product is probably susceptible to rearrangement.

$$C_6H_5N_3 + PH_3 \longrightarrow \{C_6H_5N{=}PH_3\} + N_2 \longrightarrow C_6H_5NH{-}PH_2$$

No results have as yet been published on the reactivity of azides toward diphosphines, which are known to be prone to rearrangements originating in the breaking of the phosphorus–phosphorus bond.[6]

The present work was thus undertaken to investigate the behavior of the two different types of phosphines toward triphenylsilyl azide.

Tetraphenyldiphosphine was prepared following the procedure of Kuchen and Buchwald;[7] however, the product exhibited a somewhat different infrared spectrum from that reported by the above-mentioned authors. Of special significance is the weakness of the absorption in our spectrum at 1180 cm^{-1}, where a strong band was observed by Kuchen and Buchwald. We attribute the absorption at 1180 cm^{-1} to the presence of the oxide.[8,9] Since other analytical data given by these authors show their material to be pure, we believe that oxidation evidenced in their infrared spectrum occurred during either sample preparation or the actual recording of the spectrum.

Interaction of tetraphenyldiphosphine with triphenylsilyl azide afforded the desired doubly oxidized

$$\underset{\text{I}}{(C_6H_5)_3SiN{=}P(C_6H_5)_2P(C_6H_5)_2{=}NSi(C_6H_5)_3}$$

product I. No other material was isolated from the reaction mixture.

The reaction of diphenylphosphine with triphenylsilyl azide did not proceed very readily. From the equimolar reaction mixture two products were isolated with Si:P ratios of 1:1 and 2:1. The reaction sequence can be best explained by the equation depicted below, wherein the monoadduct II reacts with an additional mole of silyl azide to give compound III, which now

$$(C_6H_5)_2PH + (C_6H_5)_3SiN_3 \longrightarrow \underset{\text{II}}{(C_6H_5)_3SiNHP(C_6H_5)_2} \xrightarrow{(C_6H_5)_3SiN_3} \underset{\text{III}}{(C_6H_5)_3SiNHP(C_6H_5)_2{=}NSi(C_6H_5)_3}$$

contains the phosphorus in a pentavalent state. The second step appears to proceed more readily than the first step, since even though equimolar quantities of triphenylsilyl azide and diphenylphosphine were employed a 45% yield of the disubstituted material was isolated together with unreacted diphenylphosphine. If the reaction is conducted using an excess of triphenylsilyl azide only the diadduct is obtained. The proposed structures of compounds II and III are based on their infrared and P^{31} nmr spectra. The presence in compound II of a weak but sharp absorption at 3315 cm^{-1} in conjunction with a strong absorption at 905 cm^{-1} [10,11] points to the presence of the P–NH moiety. This is further supported by the absence of characteristic P–H absorption at 2440–2350 cm^{-1} and the lack of splitting in P^{31} nmr, which would be expected from a P–H group. The formation of $(C_6H_5)_3SiNHP(C_6H_5)_2{=}NSi(C_6H_5)_3$ is an additional proof of the proposed structure for compound II, since in $(C_6H_5)_3SiN{=}P(H)(C_6H_5)_2$ the phosphorus is already in a pentavalent state. The postulated structure of the diadduct III is again in agreement with its infrared and P^{31} nmr spectra (sharp band at 3315 cm^{-1}, strong absorption at 935 cm^{-1}, no absorption at 2440–2350 cm^{-1}, and lack of splitting in the nmr).

Reactions of other types of azido compounds with diphenylphosphine and other secondary phosphines are currently being investigated in order to elucidate the mechanism which leads to the formation of $(C_6H_5)_3SiNHP(C_6H_5)_2$ (II). This reaction is probably an exchange process with a peculiar mechanism due to the electronegativities involved, or a complex oxidation–reduction reaction involving more diphenylphosphine than stoichiometrically required.

Experimental Section

The reactions were conducted either in a vacuum system or in a nitrogen atmosphere with rigid exclusion of moisture and oxygen. All chemicals were purified by applicable methods. Triphenylsilyl azide, mp 84.5–85.5°, was prepared in 83% yield following the procedure of Wiberg, *et al.*;[3] diphenylphosphine, bp 163–163.5° (14.8 mm), was obtained by the method of Kuchen and Buchwald[7] in 51% yield. Melting points were determined in sealed capillaries and are uncorrected. The infrared spectra were recorded on a Perkin-Elmer double-beam (Model 21) infrared

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[1] MHD Research, Inc., Newport Beach, Calif. 92663.

[2] R. West and J. S. Thayer, *J. Am. Chem. Soc.*, **84**, 1763 (1962).

[3] N. Wiberg, F. Raschig, and R. Sustmann, *Angew. Chem. Intern. Ed. Engl.*, **1**, 551 (1962).

[4] R. H. Kratzer and K. L. Paciorek, *Inorg. Chem.*, **4**, 1767 (1965).

[5] H. Staudinger and E. Hauser, *Helv. Chim. Acta*, **4**, 861 (1921).

[6] R. S. Hayter and L. F. Williams, *Inorg. Chem.*, **3**, 717 (1964), and references cited therein.

[7] W. Kuchen and H. Buchwald, *Chem. Ber.*, **91**, 2871 (1958).

[8] The infrared spectrum of $(C_6H_5)_2P(O)P(O)(C_6H_5)_2$, given by Kuchen and Buchwald,[7] exhibits a very strong band at 1180 cm^{-1}.

[9] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1956, p 312, reports absorption in the vicinity of 1200 cm^{-1} for phosphine oxides.

[10] $(C_6H_5)_2P(O)NH_2$ exhibits a strong absorption at 910 cm^{-1}: K. L. Paciorek and R. H. Kratzer, unreported results.

[11] E. Steger, *Chem. Ber.*, **94**, 266 (1961).