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Thiophosphate Chemistry.[1] The Anion Set $X_2PS_2^-$, $(XPS_2)_2S^{2-}$, and $(XPS_2)_2S_2^{2-}$

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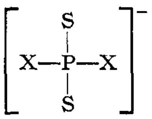
Nucleophilic attack of P_4S_{10} by anions yielded the novel thiophosphates $F_2PS_2^-$, $(FPS_2)_2S^{2-}$, $(FPS_2)_2S_2^{2-}$, $(N_3)_2PS_2^-$, $(N_3PS_2)_2S^{2-}$, $(NC)(H_2NSC)PS_2^-$, $(NCPS_2)_2S^{2-}$, and $(NCS)_2PS_2^-$ [or $(SCN)_2PS_2^-$]. The $F_2PS_2^-$ ion has a rich chemistry yielding the strong, volatile acid $HSPSF_2$, $RSPSF_2$ from alkyl halides, $(F_2PS_2)_2$ by bromine oxidation, and metal chelates.[2,3] Reaction of $(N_3)_2PS_2^-$ with P_4S_{10} yielded the ion $P_4S_9N^-$ which is a structural analog of P_4S_{10}.

Introduction

Tetraphosphorus decasulfide is subject to general degradation by nucleophiles. We have found anionic (X^-) attack of the decasulfide to produce a number of new thiophosphate ions of the classes $X_2PS_2^-$, $XYPS_2^-$, $(XPS_2)_2S^{2-}$, and $(XPS_2)_2S_2^{2-}$. Some of these ions, particularly $F_2PS_2^-$, have an extensive chemistry. We also describe a new ion $P_4S_9N^-$ with the adamantyl structure.

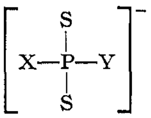
Results and Discussion

Preparation of the Thiophosphate Ions.—Reaction of tetraphosphorus decasulfide with alkali metal salts of fluoride, azide, cyanide, and thiocyanate ions occurs in solvents such as acetonitrile, 1,2-dimethoxyethane, or water to give a variety of ionic products. Reactions are fast, in some cases exothermic, despite the fact that the sulfide and the salts (in organic media) have low solubilities. Four classes of products were isolated, *i.e.*



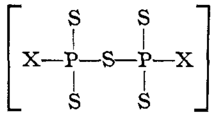
$$\left[X\!-\!\overset{\displaystyle S}{\underset{\displaystyle S}{P}}\!-\!X \right]^-$$

I



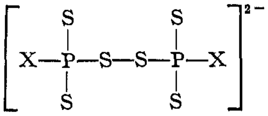
$$\left[X\!-\!\overset{\displaystyle S}{\underset{\displaystyle S}{P}}\!-\!Y \right]^-$$

II



$$\left[X\!-\!\overset{\displaystyle S}{\underset{\displaystyle S}{P}}\!-\!S\!-\!\overset{\displaystyle S}{\underset{\displaystyle S}{P}}\!-\!X \right]^{2-}$$

III



$$\left[X\!-\!\overset{\displaystyle S}{\underset{\displaystyle S}{P}}\!-\!S\!-\!S\!-\!\overset{\displaystyle S}{\underset{\displaystyle S}{P}}\!-\!X \right]^{2-}$$

IV

Product distribution and yields were sensitive to reaction conditions, especially the reaction medium, and to the work-up method.

Class I ions are predominant products except in the sodium cyanide reaction where no class I ion was isolated; $(NCPS_2)_2S^{2-}$ was the major cyano derivative, and a class II ion, $(NC)(H_2NC(S))PS_2^-$, was a minor product ostensibly arising from H_2S (a hydrolytic impurity) addition to $(NC)_2PS_2^-$.[4] In these reactions, yields of class I–III ions never exceeded 22%. The fate of the remaining phosphorus species was not definitely established although apparently complex thiophosphates of the empirical compositions $P_2S_8^{2-}$ and $P_2S_{10}^{2-}$ were formed. Whether the yields are mechanistically limited to about one-fourth of the phosphorus content of the tetraphosphorus decasulfide molecule was not established.

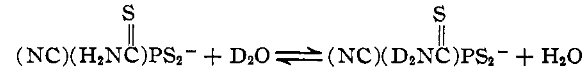
An alternative and better route to $F_2PS_2^-$ was found in the quantitative reaction

$$2CsF + 2PSF_3 \longrightarrow CsPF_6 + CsF_2PS_2$$

Thiophosphoryl fluoride was prepared in high yield by the hydrogen fluoride degradation of P_4S_{10}

$$12HF + P_4S_{10} \longrightarrow 4PSF_3 + 6H_2S$$

Characterization of the Ions.—Identity of the ions was established by composition in several representative salts, by spectral data, and for $F_2PS_2^-$ by its diverse derivative chemistry.[1–3] One ion, $(NC)(H_2NC(S))PS_2^-$, justifies further comment in this section. The thioamide formulation is based on infrared and nmr studies of the ion and the deuterio analog generated by the exchange reaction



$$(NC)(H_2N\overset{\displaystyle S}{\overset{\|}{C}})PS_2^- + D_2O \rightleftharpoons (NC)(D_2N\overset{\displaystyle S}{\overset{\|}{C}})PS_2^- + H_2O$$

The N–H stretching and bending modes of the ion shifted on deuteration from 3300, 3200, 3120, and 1585 to 2480, 2315, and 1128 cm^{-1}, and the ^{31}P multiplet reduced to a single sharp line. The $C\equiv N$ stretching mode was at 2170 cm^{-1}. Proton nmr showed the NH protons to be 2 in number and to be nonequivalent, presumably because of restricted rotation about the CN bond as is commonly found in amides and thioamides. One NH proton resonance was a broad doublet (J_{PH} = 40 Hz) and the other a broad unresolved peak. The ^{31}P nmr showed phosphorus coupling with both protons (J_{PH} = 40 and 6.7 Hz). Fast rotation relative to nmr time at 120° was signaled by the collapse of the phosphorus spectrum to a multiplet, transitional to the limiting triplet ($J \approx 24$ Hz).

Fluorine and phosphorus nmr spectra of $(FPS_2)_2S^{2-}$ showed only one type of fluorine and phosphorus. Fine structure was characteristic of an AA′XX′ pattern. These data support the symmetrical type-III structure.

Chemical Properties.—Hydrolytic stability of $F_2PS_2^-$ is high and the conjugate acid has been isolated in pure

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[1] A preliminary account has appeared: H. W. Roesky, F. N. Tebbe, and E. L. Muetterties, *J. Am. Chem. Soc.*, **89**, 1272 (1967).

[2] F. N. Tebbe, H. W. Roesky, W. C. Rode, and E. L. Muetterties, *ibid.*, **90**, 3578 (1968).

[3] F. N. Tebbe and E. L. Muetterties, *Inorg. Chem.*, **9**, 629 (1970).

[4] H. W. Roesky, *Chem. Ber.*, **100**, 2138 (1967), has successfully isolated salts of the parent $(NC)_2PS_2^-$ ion.

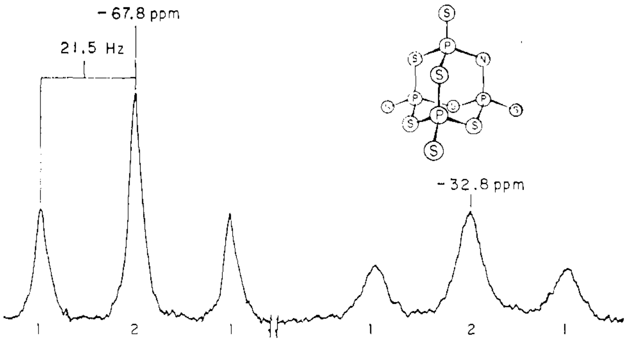

Figure 1.—The ^{31}P nmr spectrum and proposed structure of $(n\text{-}C_3H_7)_4NP_4S_9N$.

form.[2,5] The acid has a $pK_a = 1.0$, comparable to oxalic acid, and it is quite volatile (bp 72° (760 mm)). Thermal stability is variable depending upon the associated cation. For CsF_2PS_2, degradation under vacuum is immeasurable at 275°, slow at 300°, and moderately fast at 375°. Gaseous products are PSF_3 and PF_3 in ~3:1 molar ratio. Oxidation of the ion with bromine occurs at 25° to give $F_2(S)PSSP(S)F_2$.

Alkyl halides react with CsF_2PS_2 to give the respective alkyl difluorodithiophosphates $RSPSF_2$ as demonstrated for the ethyl, isopropyl, and benzyl halides. The disulfide, $F_2(S)PSSP(S)F_2$, thermally adds to olefins; *e.g.*, cyclohexene yields $C_6H_{10}(SPSF_2)_2$ at ~80°.

The $P_4S_9N^-$ Ion.—Tetraphosphorus decasulfide reacts with $(N_3)_2PS_2^-$ with sulfur substitution by nitrogen[6] to form $P_4S_9N^-$. The infrared spectra of salts show a strong band at 1180 cm^{-1}, a region characteristic[7] of the multiply linked PN in phosphonitrilic compounds. In the ^{31}P spectrum, there are two triplets of equal intensity, one broader than the other. A structure (Figure 1) based on the established P_4S_{10} adamantane-like cage is consistent with the nmr data which show two sets of phosphorus atom environments. The broader ^{31}P triplet may represent the two phosphorus atoms in proximity to the quadrupolar nitrogen nucleus.

There must be significant charge delocalization within the $P_4S_9N^-$ ion since alkylation did not occur even with reagents like dimethyl sulfate.

Experimental Section

General Procedures.—Tetraphosphorus decasulfide and polyphosphoric acid were used as received from Stauffer Chemical Co. Acetonitrile and 1,2-dimethoxyethane were dried over molecular sieves prior to use. Product salts were dried over phosphorus pentoxide under *ca.* 1 μ pressure. Fluorine nmr spectra are reported with reference to fluorotrichloromethane contained, unless otherwise stated, in the solution. Phosphorus nmr spectra are reported with reference to external 85% phosphoric acid.

Preparation of SPF_3.—Hydrogen fluoride, approximately 10 g (0.5 mol), and 11 g (0.025 mol) of tetraphosphorus decasulfide were heated in a Hastelloy-C pressure vessel for 8 hr at 200°. The product, thiophosphoryl fluoride, was purified by passage through a −80° trap under vacuum. The yield was 8.5 g (71% based on P). The yield was 3.9 g (33%) when this experiment was conducted at 180°.

CsF_2PS_2 from SPF_3 and CsF.—A 1-l. flask was equipped with a stirrer, thermometer, gas inlet tube, and an exit port fitted with a water-cooled condenser followed in series by a Dry Ice cooled condenser. A bubbler containing aqueous sodium hydroxide which was vented to a hood was provided for exit gases. A trap was included to prevent accidental contact of water with the reagents in the flask. Provision was made for sweeping the entire apparatus with dry nitrogen. The flask was charged with 53 g (0.35 mol) of cesium fluoride (dried at 100°, 0.1 μ) and 200 ml of anhydrous acetonitrile. Air was thoroughly purged from the system and 42 g (0.35 mol, bp −50 to −48°) of thiophosphoryl fluoride[8] from a stainless steel storage cylinder was admitted to the flask above the level of the stirred suspension at a rate slow enough so that excess gas did not reach the Dry Ice condenser. The temperature was not allowed to rise above 45°. The addition required approximately 30 min. (*Caution!* Thiophosphoryl fluoride inflames and forms explosive mixtures with air. No more than the required amount of gas should be introduced.) After the reaction was complete, the system was thoroughly purged with nitrogen and the product mixture was filtered. The white insoluble solid, washed 3 times with 20-ml portions of acetonitrile and dried under vacuum at 100°, weighed 40 g and was identified as $CsPF_6$ by the ^{19}F nmr spectrum and elemental analyses. *Anal.* Calcd for CsF_6P: F, 41.0; P, 11.2. Found: F, 41.1; P, 10.9 (S, 0.3).

Solvent was removed from the filtrate and washed and the residue was dried under vacuum to a weight of 52 g. By nmr analysis this material consisted of CsF_2PS_2 contaminated with approximately 5 g of $CsPF_6$ and traces of other impurities. The total yield of $CsPF_6$ was thus 45 g (93%). The impure sample was dissolved in 75 ml of 2-butanone at 25° and filtered through diatomaceous earth. The filter cake was washed with two 5-ml portions of solvent. Solvent was removed from the combined filtrates to yield an off-white solid which was dried at 60° under vacuum. The yield was 42 g (90%) of CsF_2PS_2 contaminated with approximately 0.6 mol % of $CsPF_6$. *Anal.* Calcd for CsF_2PS_2: Cs, 50.0; F, 14.3; P, 11.6; S, 24.1. Found: Cs, 49.8; F, 14.3; P, 12.0; S, 24.0. The compound was further purified by recrystallization under nitrogen from absolute ethanol using ~100 ml of solvent for 30 g of product. Two-thirds of the material was recovered in the first crop. After four such recrystallizations the compound was white and free of hexafluorophosphate. It melted to a yellow liquid over the range 326–334°. *Anal.* Found: Cs, 49.6; F, 14.4; P, 11.7; S, 24.8. Ir (acetone): 815, 781, 730 cm^{-1}; ^{19}F nmr $((CH_3)_2SO)$: δ 1.4 (d, $J_{PF} = 1152$ Hz); ^{31}P nmr $((CH_3)_2SO)$: δ −116 (t, $J_{PF} = 1161$ Hz).

Cesium difluorodithiophosphate dissolves easily in solvents such as water, acetonitrile, and lower alcohols and ketones. It was stable in aqueous solutions of pH 1–10 for 1 week at room temperature.

$F_2PS_2^-$ from P_4S_{10} and F^-.—A mixture of sodium fluoride, 2.5 g (0.06 mol), and P_4S_{10}, 4.4 g (0.01 mol), in 50 ml of acetonitrile was stirred for 0.5 hr at 80°. The solution was allowed to cool to room temperature and was filtered. Solvent was removed under vacuum at room temperature. The resulting product was dissolved in 20 ml of water saturated with sodium

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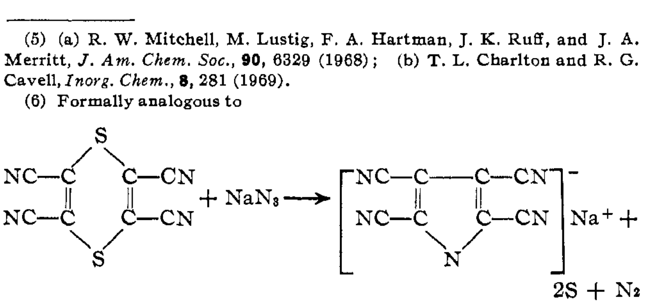
[5] (a) R. W. Mitchell, M. Lustig, F. A. Hartman, J. K. Ruff, and J. A. Merritt, *J. Am. Chem. Soc.*, **90**, 6329 (1968); (b) T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **8**, 281 (1969).

[6] Formally analogous to



See H. E. Simmons, Jr., U. S. Patent 3,221,024 (1965), and H. E. Simmons and R. D. Vest, unpublished information.

[7] See D. E. C. Corbridge in "Topics in Phosphorus Chemistry," Vol. 3, E. J. Griffith and M. Grayson, Ed., Interscience Publishers, New York, N. Y., 1966, p 334.

[8] C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **25**, 2016 (1960).

fluoride. The anion isolated as the tetra-*n*-propylammonium salt weighed 2.6 g (20% based on phosphorus) and was identified by its melting point and ir and ^{19}F nmr spectra as described below.

$F_2PS_2^-$, $(n\text{-}C_3H_7)_4N^+$, $(n\text{-}C_4H_9)_4N^+$, and $(C_6H_5)_3PCH_3^+$ Salts.—The $F_2PS_2^-$ ion was recovered nearly quantitatively from aqueous solution by precipitation with organosubstituted ammonium, phosphonium, or arsonium cations. For example, a solution of 4.00 g (0.0150 mol) of tetra-*n*-propylammonium bromide in 30 ml of water was added to a stirred solution of 3.00 g (0.0113 mol) of CsF_2PS_2 in 30 ml of water. The white precipitate was collected, washed three times with 10-ml portions of water and with ether, and dried at room temperature under vacuum. The yield was 3.47 g (96%), mp 161°. The sample was dissolved in a solution of 35 ml of methanol and 10 ml of water and chilled to 0° to effect recrystallization. The white crystalline solid was dried under vacuum. Recovery was 2.2 g, mp 164°. *Anal.* Calcd for $C_{12}H_{28}F_2NPS_2$: C, 45.1; H, 8.8; F, 11.9; N, 4.4; P, 9.7; S, 20.1. Found: C, 45.1; H, 9.0; F, 11.6; N, 4.3; P, 9.5; S, 20.0. Characteristic bands in the 807–200-cm^{-1} region of the infrared spectrum were at 807 (s), 778 (s), 725 (s), 552 (m), 388 (m), 361 (s), 313 cm^{-1} (w); ^{19}F nmr (CH_3CN): δ 2.3 (d, J_{PF} = 1150 Hz); ^{31}P nmr (CH_3CN): δ −118 (t).

The tetra-*n*-butylammonium salt, mp 208–209°, was similarly prepared and purified. *Anal.* Calcd for $C_{16}H_{36}F_2NPS_2$: C, 51.2; H, 9.7; P, 8.3; S, 17.1. Found: C, 51.1; H, 9.6; P, 8.3; S, 17.1. The triphenylmethylphosphonium salt similarly prepared and recrystallized from methanol melted at 139–140°. *Anal.* Calcd for $C_{19}H_{18}F_2P_2S_2$: C, 55.6; H, 4.4; F, 9.3; P, 15.1; S, 15.6. Found: C, 55.8; H, 4.4; F, 9.5; P, 15.2; S, 15.9.

$(FPS_2)_2S^{2-}$ and $(FPS_2)_2S_2^{2-}$, $(n\text{-}C_3H_7)_4N^+$ Salts.—A suspension of P_4S_{10} (100 g, 0.23 mol) and sodium fluoride (57 g, 1.4 mol) in 900 ml of 1,2-dimethoxyethane was prepared at room temperature and stirred under nitrogen. The temperature of the mixture increased to 50° over 50 min. Heat was supplied to bring the mixture, over 25 min, to the reflux temperature. The mixture was then cooled and solvent removed at room temperature under vacuum. The resulting brownish oil was dissolved in 700 ml of water at 0°. Precipitation of the products from aqueous solution by stepwise addition of tetrapropylammonium cation allowed separation of the apparently more soluble $(FPS_2)_2S^{2-}$ ion from oily by-products and $[(n\text{-}C_3H_7)_4N]_2(FPS_2)_2S_2$. A chilled solution of 50 g of tetra-*n*-propylammonium bromide in 100 ml of water was added to the solution. The resulting low-melting solid was filtered off and washed with water and with ether. Work-up of the filtrate is described below. The low-melting solid was slurried with 150 ml of methanol at room temperature and the insoluble fraction was collected and dried under vacuum. The yield of crude $[(n\text{-}C_3H_7)_4N]_2(FPS_2)_2S_2$ was 8.8 g (3% based on phosphorus). This material was twice recrystallized from methanol–acetonitrile solution and twice from acetonitrile to a melting point of 217–218°. *Anal.* Calcd for $C_{24}H_{56}F_2N_2P_2S_6$: C, 43.3; H, 8.5; F, 5.7; N, 4.2; P, 9.3; S, 28.9. Found: C, 43.3; H, 8.1; F, 5.7; N, 4.2; P, 9.3; S, 29.3. Ir (800–400 cm^{-1}): 777 (m), 767 (m), 755 (m), 699 (s), 580 (w), 556 (s), 447 cm^{-1} (m); ^{19}F nmr (CH_3CN): δ −7.4 (d, J_{PF} = 1170 Hz).

The filtrate described above containing the $(FPS_2)_2S^{2-}$ ion was treated with 25 g of tetra-*n*-propylammonium bromide dissolved in 50 ml of water. The resulting white precipitate weighed, after drying under vacuum, 23 g (8% yield based on phosphorus), mp 204–206°. Methanol solutions of the salt prepared at room temperature were chilled to 0° to effect crystallization. After four recrystallizations the melting point was 205°. *Anal.* Calcd for $C_{24}H_{56}F_2N_2P_2S_5$: C, 45.5; H, 8.9; F, 6.0; N, 4.4; P, 9.8; S, 25.3. Found: C, 45.5; H, 8.6; F, 6.4; N, 4.4; P, 9.8; S, 25.7. Ir (800–400 cm^{-1}): 770 (s), 758 (s), 704 (vs), 688 (s), 537 (vs), 442 cm^{-1} (s); ^{19}F nmr (CH_3CN, 80°): δ −7.6 (complex d, J_{PF} = 1160 Hz); ^{31}P nmr (CH_3CN, 80°): δ −115 (complex d, J_{PF} = 1151 Hz).

The $(FPS_2)_2S^{2-}$ anion was also isolated in small yield from reaction of phosphorus pentasulfide and sodium fluoride in an aqueous medium. Phosphorus pentasulfide, 40 g, was added to a slurry of 50 g of sodium fluoride in 500 ml of water. The mixture was stirred rapidly for 1.5 hr. Solids were filtered off and a solution of 20 g of tetra-*n*-propylammonium bromide was added to the filtrate. The resulting mixture of solid products was dried under vacuum. The quantity of solid isolated was 21 g. This mixture once recrystallized from methanol–water solution yielded 3 g of material, mp 185–188°, with the characteristic infrared spectrum of $[(n\text{-}C_3H_7)_4N]_2[(FPS_2)_2S]$. The salt was further purified by recrystallization to a melting point of 205°. Identification of the product was confirmed by elemental analyses.

$(N_3)_2PS_2^-$, $(n\text{-}C_3H_7)_4N^+$, and $(C_6H_5)_3CH_3P^+$ Salts.—A suspension of tetraphosphorus decasulfide (5.5 g, 0.012 mol) and sodium azide (4.8 g, 0.074 mol), corresponding to an azide to tetraphosphorus decasulfide ratio of 6:1, in 50 ml of acetonitrile was stirred at the reflux temperature for 1.3 hr. The work-up procedure was conducted in a well-ventilated hood. Insolubles were filtered off and solvent was removed from the filtrate at room temperature and 1 μ pressure. The resulting solid product was chilled to 0° and 25 ml of water (0°) was added. The mixture was continuously purged with a stream of nitrogen to remove hydrazoic acid as it was produced. After an initial vigorous reaction the mixture was warmed to room temperature and allowed to stand 14 hr. The filtered solution was treated with 7.5 g of tetra-*n*-propylammonium bromide dissolved in 15 ml of water. A white precipitate was isolated, washed with water and with ether, and dried at room temperature under vacuum. The yield was 4.0 g (0.011 mol) or 22% based on phosphorus. The quantity of sodium azide was varied in the above procedure from an azide:tetraphosphorus decasulfide molar ratio of 2:1 to 8:1. Yields were, respectively, 3 and 17%. The salt, three times recrystallized from methanol–water solutions, melted at 75–77°. *Anal.* Calcd for $C_{12}H_{28}N_7PS_2$: C, 39.4; H, 7.7; N, 26.8; P, 8.5; S, 17.5. Found: C, 39.5; H, 7.8; N, 26.6; P, 8.6; S, 17.7. Ir: 2100 (s, asym N_3 str) and 1230 cm^{-1} (s, sym N_3 str), and, in the 738–200-cm^{-1} region, 738 (s), 703 (s), 679 (s), 579 (s), 555 (w), 512 (s), 468 (w), 338 (w), 318 cm^{-1} (w); ^{31}P nmr (CH_3CN, 80°): δ −95.6 (broad s). The anion was also isolated as the triphenylmethylphosphonium salt using the above procedure. The salt was recrystallized from methanol, mp 75–77°. *Anal.* Calcd for $C_{19}H_{18}N_6P_2S_2$: C, 50.0; H, 4.0; N, 18.4; P, 13.6; S, 14.1. Found: C, 49.6; H, 3.9; N, 17.9; P, 13.4; S, 14.5.

The reaction has been carried out on a scale 4 times that described. The acetonitrile solution containing the product mixture was, however, divided into parts comparable in size to that described above and the parts were treated separately. The purified tetra-*n*-propylammonium salt was not shock sensitive. An attempt to isolate the cesium salt of $(N_3)_2PS_2^-$ resulted in an explosion. An aqueous solution of the sodium salt, prepared as described above, was passed through an acidic ion-exchange column. The eluent was neutralized with cesium hydroxide and water was removed from the solution until crystallization began to take place. Some of the crystals detonated as they formed.

$(N_3PS_2)_2S^{2-}$, $(n\text{-}C_3H_7)_4N^+$ Salt.—A mixture of sodium azide, 25 g (0.38 mol), and P_4S_{10}, 15 g (0.034 mol), in 300 ml of water was stirred rapidly for 30 min. Hydrazoic acid and hydrogen sulfide were generated. A rapid flow of nitrogen through the reaction vessel was provided to remove hydrazoic acid as it was evolved. The mixture was filtered and 25 g of tetra-*n*-propylammonium bromide in 50 ml of water was added to the filtrate to precipitate 12 g of crude product mixture. This solid was separated into two fractions by extraction with 40 ml of methanol at room temperature. Two grams of $(n\text{-}C_3H_7)_4N(N_3)_2PS_2$ was isolated from the soluble fraction. The insoluble fraction, 3.3 g, was isolated and recrystallized once from methanol (mp 152–155°), and 3 times from anhydrous acetonitrile to a melting point of 154–155 dec. *Anal.* Calcd for $C_{24}H_{56}N_8P_2S_5$: C, 42.5; H, 8.3; N, 16.5; P, 9.1; S, 23.6. Found: C, 42.5; H, 8.1; N, 16.3; P, 9.2; S, 23.7. Ir: 2110 (s, asym N_3 str), 1243 cm^{-1} (s, sym

N_3 str), and, in the 800–400-cm^{-1} region, 763 (sh), 753 (m), 721 (s), 710 (s), 682 (s), 672 (s), 565 (s), 525 (m), 483 (s), 435 cm^{-1} (m); ^{31}P nmr (CH_3CN, 80°): δ −92.4 (broad s).

$FN_3PS_2^-$, $(n\text{-}C_3H_7)_4N^+$ Salt.—A solution of 2 g of $(n\text{-}C_3H_7)_4N(N_3)_2PS_2$ in 25 ml of methanol and 5 ml of water was treated with 10 ml of a 10% hydrofluoric acid solution and allowed to stand for 2 days. The product was recrystallized from a methanol–water solution. The yield was 1.1 g, mp 94–95°. *Anal.* Calcd for $C_{12}H_{28}FN_4PS_2$: C, 42.1; H, 8.2; F, 5.5; N, 16.4; P, 9.0. Found: C, 41.5; H, 8.1; F, 5.6; N, 16.1; P, 8.9.

The tetra-*n*-propylammonium salt of $FN_3PS_2^-$ decomposes slowly at ~110° to form brown products.

When 25% aqueous hydrofluoric acid was used in the above procedure, further substitution yielded the $F_2PS_2^-$ ion.

$(NC)(H_2NSC)PS_2^-$ and $(NCPS_2)_2S^{2-}$, $(n\text{-}C_3H_7)_4N^+$ Salts.—Tetraphosphorus decasulfide, 264 g (0.59 mol), and sodium cyanide, 300 g (6.1 mol), were suspended in 2400 ml of acetonitrile. The mixture was rapidly stirred for 35 min. The heat of reaction warmed the mixture to 52°. The solution was filtered under nitrogen and the filtrate was divided into four equal portions which were worked up separately. Quantities described below apply to one portion. Solvent was removed under vacuum at room temperature and the resulting glassy solid was chilled to 0° and dissolved in 200 ml of ice water. A chilled solution of 50 g of tetra-*n*-propylammonium bromide in 75 ml of water was added and the resulting yellow precipitate was filtered off, washed twice with 100-ml portions of water, washed with ether, and placed in 1 l. of methanol to stand for 14 hr. The off-white insoluble portion consisting primarily of the $(NCPS_2)_2S^{2-}$ salt was isolated and washed with 600 ml of methanol. The combined methanol filtrates were reduced in volume and chilled to precipitate the yellow tetra-*n*-propylammonium salt of $(NC)(H_2NSC)PS_2^-$. The salts were dried under vacuum at room temperature. Yields for the four portions combined were 94 g (12% based on P), mp 203°, of $[(n\text{-}C_3H_7)_4N]_2(NCPS_2)_2S$ and 79 g (9%), mp 117–121°, of $(n\text{-}C_3H_7)_4N(NC)(H_2NSC)PS_2$.

The rate of this reaction depends on the particle size of the reagents. Yields varied with the work-up procedure. When water contacted the crude mixture of sodium salts at room temperature, an exothermic reaction destroyed most of the reported products. In one experiment use of a smaller relative quantity of sodium cyanide favored the yield of the $(NCPS_2)_2S^{2-}$ ion over $(NC)(H_2NSC)PS_2^-$. Use of 1,2-dimethoxyethane as solvent for the reaction gave comparable results.

The tetra-*n*-propylammonium salt of $(NCPS_2)_2S^{2-}$ was purified by three recrystallizations from acetonitrile–methanol solutions to produce large white crystals, mp 202–203°. *Anal.* Calcd for $C_{26}H_{56}N_4P_2S_5$: C, 48.3; H, 8.7; N, 8.7; P, 9.6; S, 24.8. Found: C, 48.2; H, 8.5; N, 8.4; P, 9.5; S, 24.8. Raman (methanol–dimethyl sulfoxide): 2160 cm^{-1} (C–N str); ir (760–400-cm^{-1} region): 752 (s), 708 (s), 695 (s), 755 (m), 710 (s), 698 (s), 596 (s), 555 (w), 506 (s), 426 cm^{-1} (m); ^{31}P nmr (acetonitrile, 80°): δ −35.1 (s).

The thioamide salt was recrystallized from methanol and methanol–water solutions to a melting point of 120–122°. *Anal.* Calcd for $C_{14}H_{30}N_3PS_3$: C, 45.8; H, 8.2; N, 11.4; P, 8.4; S, 26.2. Found: C, 45.8; H, 7.9; N, 11.4; P, 8.7; S, 26.1; ir (Nujol, 3300–1585 cm^{-1}): 3300, 3200, and 3120 cm^{-1} (N–H str), 1585 cm^{-1} (N–H def); ir (KBr, 700–400 cm^{-1}): 700 (s), 622 (s), 587 (w), 484 cm^{-1} (w); Raman: 2170 cm^{-1} (C–N str); ^1H nmr (acetone-d_6): δ 9.46 (broad d, $J_{PH(1)} = 40$ Hz, $C(S)NH(1)H(2)$), δ 9.2 (broad single peak without resolved structure, $C(S)NH(1)H(2)$), integrated area of $NH(1) + NH(2) \sim 1.6$, δ 3.37 (multiplet, area 8, $CH_2CH_2CH_3$), δ 1.80 (multiplet, area 8, $CH_2CH_2CH_3$), δ 1.02 (multiplet, area 12, $CH_2CH_2CH_3$); ^{31}P nmr (acetonitrile, 80°): δ −51.2 (doublet, $J_{H(1)P} = 40$ Hz, of doublets, $J_{H(2)P} = 6.7$ Hz).

$(NC)(H_2NSC)PS_2^-$-d_2.—Three grams of $(n\text{-}C_3H_7)_4N(NC)(H_2NSC)PS_2$ in 6 ml of acetonitrile was shaken with 5 ml of deuterium oxide. The layers were separated, acetonitrile was added to replace that extracted into the water, and the exchange was repeated 4 times. Solvent was removed at room temperature and the yellow product dried at 56° to a melting point of 120–121°. The infrared spectrum contained no absorptions characteristic of the isotopically normal compound at 3300, 3200, 3120, and 1585 cm^{-1} and contained new absorptions at 2480, 2315, and 1128 cm^{-1} attributed to N–D vibrations. The ^{31}P nmr spectrum of the deuterated material (acetonitrile solvent, 80°) consisted of a single sharp line at −51.5 ppm. On exposure of the sample to the moisture of the air deuterium was exchanged for hydrogen.

$(NCS)_2PS_2^-$ or $(SCN)_2PS_2^-$, $(n\text{-}C_3H_7)_4N^+$ Salt.—A suspension of 180 g (0.40 mol) of tetraphosphorus decasulfide and 160 g (1.6 mol) of potassium thiocyanate in 1 l. of acetonitrile was stirred rapidly for 2.5 hr. The product, in solution, was filtered off and solvent was removed under vacuum. To the residue was added a solution, chilled to 0°, of 100 g of tetra-*n*-propylammonium bromide in 400 ml of water. The mixture was stirred and the precipitated alkylammonium salt was isolated and washed with water and with ether. An absolute ethanol–petroleum ether (bp 30–60°) solution of the salt, prepared at room temperature, was chilled to 0° to accomplish recrystallization. The product was degraded by warm alcohol. The yield of recrystallized material was 97 g (15% based on P), mp 76–78°. After four further recrystallizations the melting point of the pale yellow material was 75–77°. *Anal.* Calcd for $C_{14}H_{28}N_3PS_4$: C, 42.3; H, 7.1; N, 10.6; P, 7.8; S, 32.3. Found: C, 41.9; H, 7.8; N, 10.5; P, 7.5; S, 31.9; ir: 2040 (s), 1995 (s), and 1930 cm^{-1} (s, SCN) and, in the 800–400-cm^{-1} region, 602 (s), 449 (s, b), 428 cm^{-1} (s, b); ^{31}P nmr (CH_3CN): δ −51.6 (s).

$P_4S_9N^-$, $(n\text{-}C_3H_7)_4N^+$ Salt.—A mixture of P_4S_{10} (19 g, 0.043 mol) and $(n\text{-}C_3H_7)_4N(N_3)_2PS_2$ (8.0 g, 0.022 mol) in 120 ml of acetonitrile was stirred 1 hr at the reflux temperature. The resulting solution was filtered at 40° and the solvent volume was reduced under vacuum. An off-white solid, mp 154–160°, crystallized from the solution and was isolated in 6.3 g (24%) yield. The salt was recrystallized once from acetonitrile and once from benzene–acetonitrile, mp 184–185°. *Anal.* Calcd for $C_{12}H_{28}N_2P_4S_9$: C, 23.5; H, 4.6; N, 4.6; P, 20.2; S, 47.1. Found: C, 23.9; H, 4.5; N, 4.7; P, 20.0; S, 47.2. The most pronounced band in the 4000–670-cm^{-1} region of the infrared spectrum was at 1180 cm^{-1} and is assigned to the $P{-}N{=}P$ group.

The ^{31}P nmr spectrum (19.2 and 40.5 MHz, dimethylformamide solutions at 50°) consisted solely of two 1:2:1 triplets at δ −67.8 (area 1.02, $J_{PP} = 21.5$ Hz, sharp) and δ −32.8 (area 1.00, $J_{PP} = 21.5$ Hz, broad).

Binary Phosphorus Sulfide Anions.—The reaction of tetraphosphorus decasulfide with sodium azide in 1,2-dimethoxyethane also produced the $(N_3)_2PS_2^-$ anion. An additional ion or mixture of ions of variable composition, approaching $P_2S_{10}^{2-}$, was isolated from the product mixture. Tetraphosphorus decasulfide, 4.4 g (0.0099 mol), and sodium azide, 3.9 g (0.060 mol), in 50 ml of 1,2-dimethoxyethane were stirred for 15 min. The mixture was then heated at 40° for 15 min. The solution was filtered under nitrogen and solvent was removed under vacuum at room temperature. The oily residue was dissolved in water, filtered, and treated with an aqueous solution of tetra-*n*-propylammonium bromide. A white precipitate was filtered off and dissolved in 100 ml of warm methanol. The solution was cooled to room temperature and 0.8 g of a white precipitate was filtered off. The filtrate was concentrated to 20 ml, filtered, and treated with 200 ml of water to precipitate 3.0 g (21%) of $(n\text{-}C_3H_7)_4N(N_3)_2PS_2$. The 0.8-g sample of less soluble salt was twice recrystallized from methanol to a melting point of 229–230° dec. *Anal.* Calcd for $C_{24}H_{56}N_2P_2S_{10}$: C, 38.2; H, 7.5; N, 3.7; P, 8.2; S, 42.5. Found: C, 37.9; H, 7.6; N, 3.8; P, 8.3; S, 43.3. Repetitions of this experiment sometimes resulted in a product containing phosphorus and sulfur in the approximate ratio of 2:8.

The yield of binary phosphorus sulfide anions depended upon the time of exposure of the sodium salt to aqueous solution before precipitation as the tetraalkylammonium salt. None of these materials survived solution in water for 1 hr, and 1.1 g of tetraalkylammonium salt was isolated from a reaction comparable in scale to that described above, after treatment with water for 5 min.

Materials with comparable infrared spectra, melting points, and solubility characteristics were also isolated from the reaction of sodium azide with tetraphosphorus decasulfide in acetonitrile. Acetonitrile was removed at room temperature from the product mixture, and an aqueous solution of tetra-*n*-propylammonium bromide was added directly to the residue. Prior treatment of the residue with water destroyed the compounds.

Infrared spectra for the samples were essentially independent of exact composition or their method of preparation and contained absorptions in the 760–400-cm^{-1} region at 753 (m), 686 (s), 674 (s), 553 (s), 504 (w), 485 (m), and 468 cm^{-1} (w).

Thermal Decomposition of CsF_2PS_2.—Gases evolved in the thermal decomposition of CsS_2PF_2 were isolated. The temperature of a 2.62-g (9.82-mmol) sample of CsS_2PF_2 in a Hastelloy-C tube connected to a vacuum system was increased in 25° increments from 200 to 350°. The temperature was maintained at each point for 20 min. No decomposition as evidenced by gas evolution took place below 275°. Decomposition was slow at 300°. At 375° the 0.84 mmol of gas collected over 1.7 hr consisted of thiophosphoryl fluoride and phosphorus trifluoride in approximately a 3:1 ratio. Further heating at 375° for 2.5 hr generated traces of gas of approximately the same composition. An additional 1.41 mmol of gas which was evolved during further pyrolysis at 450° for 7 hr consisted of thiophosphoryl fluoride and phosphorus trifluoride in the approximate ratio of 3:5. The sample further heated at 550° for 2 hr yielded a trace of gas.

Thermal Decomposition of $(n\text{-}C_3H_7)_4N(N_3)_2PS_2$.—The tetra-*n*-propylammonium salt fused to a pale yellow liquid without evolution of nitrogen. At 100° the melt turned deep blue and nitrogen was evolved. Based on decomposition to 2 mol of nitrogen/mol of $(N_3)_2PS_2^-$, the per cent of decomposition at 101–102° as a function of time was 6% (10 min), 28% (55 min), 58% (105 min), 79% (175 min), and 95% (460 min). During decomposition the color changed from deep blue to green to brown. Attempts to isolate products from partially or wholly decomposed $(n\text{-}C_3H_7)_4N(N_3)_2PS_2$ by crystallization from methanol or acetonitrile solutions were not successful. A sample of the salt was heated at 122° for 5 min to produce a small amount of nitrogen and a deep blue melt. The melt was rapidly chilled to −196° and the esr spectrum was examined at −155°. Three signals centered at $g_1 = 2.055$, $g_2 = 2.033$, and $g_3 = 2.005$ were present. The spectrum closely resembled in appearance and position the esr spectrum of sulfur dissolved in amines,[9] with $g_1 = 2.055$, $g_2 = 2.035$, and $g_3 = 2.003$.

Thermal Decomposition of $(n\text{-}C_3H_7)_4N(NC)(H_2NSC)PS_2$.—The tetra-*n*-propylammonium salt of $(NC)(H_2NSC)PS_2^-$ is thermally unstable at temperatures slightly above its melting point. A 1.21-g (3.28-mmol) sample under vacuum heated at 133–135° liberated in 30 min 3.89 mmol of volatile material consisting primarily (~90%) of hydrogen cyanide. The balance of volatile material was carbon disulfide. On further heating at this temperature for 1 hr additional hydrogen cyanide and carbon disulfide were formed in trace (0.07-mmol) amounts.

$HSPSF_2$.—Aqueous solutions of the acid of $F_2PS_2^-$ were prepared by passing aqueous solutions of the cesium salt through acidified ion-exchange resin (Fisher Scientific Co., Rexyn 101). These solutions were concentrated by distillation at reduced pressure.

To prepare the anhydrous acid, 40 g (0.15 mol) of CsF_2PS_2, 300 g of polyphosphoric acid, and 100 ml of *n*-decane were combined in a 500-ml three-neck flask fitted with a mechanical stirrer, reflux condenser, thermometer, and nitrogen inlet. The mixture was heated at 100° with stirring for 1 hr. After the mixture had cooled, the solution was decanted and the product, 10.8 g, bp 71–72°, was distilled from solvent under nitrogen. An additional 1.7 g of acid was recovered by extraction of the residue with 100 ml of *n*-decane at 140°. The combined fractions represent a yield of 62%. A smaller scale reaction was carried out without organic solvent. Polyphosphoric acid, 160 g, and 10 g (0.037 mol) of finely ground CsF_2PS_2 were mixed in a flask affixed to a still with a water-cooled condenser. The apparatus was evacuated to a pressure of 555 mm. Product was collected as the temperature of the reaction mixture was brought to 110°. The yield was 3.02 g (60%).

The boiling point of redistilled HS_2PF_2 was 72° (760 mm). *Anal.* Calcd for HF_2PS_2: H, 0.75; F, 28.3; P, 23.1; S, 47.8; mol wt 134. Found: H, 0.87; F, 28.4; P, 22.8; S, 47.8; mol wt (mass spectrum) 134. d_4^{25} 1.4797; ir (gas): 2630 (S–H), 935, 884, 840, 812 (sh), 735 (sh), 718 cm^{-1}; ^1H nmr (neat, room temperature): δ 3.98 (s); ^{19}F nmr (neat, room temperature): δ 15.8 (d, $J_{PF} = 1214$ Hz); ^{31}P nmr (neat, room temperature): δ −82.8 (t, $J_{PF} = 1213$ Hz); p$K_a = 1.0 \pm 0.2$.

The acid is a colorless hygroscopic liquid miscible with common solvents such as saturated hydrocarbons. It dissolved in water to yield a solution from which the anion was recovered quantitatively by precipitation as the tetra-*n*-propylammonium salt.

$(F_2PS_2)_2$.—Under a nitrogen atmosphere 3.3 g (0.021 mol) of Br_2 was added over 15 min to a suspension of 11 g (0.041 mol) of CsF_2PS_2 in 60 ml of diethyl ether (dried by distillation from lithium aluminum hydride). Ether was removed under vacuum and the residue was distilled using a 12-in. spinning-band column. The product (4 g, 73%) was a pale yellow liquid, bp 56° (9 mm). *Anal.* Calcd for $F_4P_2S_4$: F, 28.6; P, 23.3; S, 48.2; mol wt 266. Found: F, 28.3; P, 23.5; S, 48.0, mol wt (cryoscopic in benzene) 260; ^{19}F nmr (neat): δ 28.6 (complex d, $J_{PF} = 1268$ Hz); ^{31}P nmr: δ −72.6 (complex t). A high-resolution mass spectrum confirmed the composition (calcd mass, 265.8294; found, 265.8281). The disulfide is reactive with air and is best handled under vacuum or dry nitrogen.

$C_2H_5SPSF_2$.—Cesium difluorodithiophosphate, 26.6 g (0.10 mol), and 11 g (0.10 mol) of ethyl bromide in 60 ml of tetramethylene sulfone were heated for 3 hr at 70–80°. Unreacted ethyl bromide and the product were removed under vacuum. The mixture was shaken for 5 min with ice water, separated from water, and dried over sodium sulfate. The mixture was distilled and the product, 9.0 g (55%), was collected at 124°. *Anal.* Calcd for $C_2H_5F_2PS_2$: C, 14.8; H, 3.1; F, 23.4; P, 19.1; S, 39.6; mol wt 162. Found: C, 15.3; H, 3.5; F, 23.0; P, 18.5; S, 39.1; mol wt (cryoscopic in benzene) 157. Ir: 893, 863, 719 cm^{-1}; ^1H nmr (neat, external TMS): δ 3.05 (d, area 2, $J_{PH} = 21$ Hz, of quadruplets, $J_{HH} = 7.4$ Hz, CH_3CH_2), 1.37 (t, area 3, $J_{HH} = 7.4$ Hz, CH_3CH_2); ^{19}F nmr (neat, external $CFCl_3$): δ 24.2 (d with poorly resolved fine structure, $J_{PF} = 1206$ Hz); ^{31}P nmr (neat): δ −96.0 (t, $J_{FP} = 1209$ Hz, of triplets, $J_{HP} = 21$ Hz).

$(CH_3)_2CHSPSF_2$.—A mixture of 14 g (0.11 mol) of isopropyl bromide, 27 g (0.10 mol) of CsF_2PS_2, and 60 ml of tetramethylene sulfone was heated at 80–100° for 5 hr. Volatile products were removed under vacuum at room temperature and shaken with ice water for 1 min. The oily liquid was separated and dried over sodium sulfate. The mixture was distilled and the product, 5 g (28%), collected at 137°. *Anal.* Calcd for $C_3H_7F_2PS_2$: C, 20.5; H, 4.0; F, 21.6; P, 17.6; S, 36.4; mol wt 176. Found: C, 20.6; H, 4.0; F, 20.2; P, 17.7; S, 36.1; mol wt (cryoscopic in benzene) 171. ^{19}F nmr (neat, external $CFCl_3$): δ 23.1 (d with poorly resolved fine structure, $J_{PF} = 1206$ Hz); ^{31}P nmr (neat): δ −94.2 (t, $J_{FP} = 1206$ Hz, of doublets, $J_{HP} = 15$ Hz).

$C_6H_5CH_2SPSF_2$.—Cesium difluorodithiophosphate, 40 g (0.15 mol), and 25.7 g (0.15 mol) of benzyl bromide in 100 ml of 2-butanone were heated at the reflux temperature for 4 hr. At room temperature the mixture was filtered and solvent was removed from the filtrate under vacuum. The residue was washed twice with water, dried over sodium sulfate, and distilled 3 times. The product, 15 g (45%), was collected at 106–109° (8 mm) or at 99° (~1 mm). *Anal.* Calcd for $C_7H_7F_2PS_2$: C, 37.5; H, 3.2; F, 17.0; P, 13.8; S, 28.6; mol wt 224. Found: C, 38.5; H, 3.4; F, 16.0; P, 13.8; S, 28.2; mol wt (cryoscopic in benzene)

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221. ^{1}H nmr (neat, external TMS): δ 6.93 (s, area 5, $C_6\mathit{H}_5$), δ 3.79 (d, area 2, J_{PH} = 18 Hz, $C_6H_5C\mathit{H}_2$); ^{19}F nmr (neat, external $CFCl_3$): δ 24.1 (d, J_{PF} = 1215 Hz, of triplets, J_{HF} = 1 Hz); ^{31}P nmr (neat): δ −93.6 (t, J_{FP} = 1215 Hz, of triplets, J_{HP} = 18 Hz).

$C_6H_{10}(SPSF_2)_2$.—A mixture of cyclohexene, 6.0 g (0.073 mol), and $(F_2PS_2)_2$, 17.2 g (0.065 mol), was heated for 4.5 hr at 83°. The mixture was distilled under nitrogen at 6 mm using a 12-in. spinning-band column. A fraction, bp 69–114° (6 mm), weighing 8.1 g was redistilled and the product was collected at 104° (0.55 mm). A small amount of higher boiling impurity present in the distillate was removed by evaporation of the product under higher vacuum (~0.1 μ) in a molecular still heated to 120°. *Anal.* Calcd for $C_6H_{10}F_4P_2S_4$: C, 20.7; H, 2.9; F, 21.8; P, 17.8; S, 36.8. Found: C, 20.9; H, 3.0; F, 22.0; P, 18.2; S, 37.3. Ir (liquid film, 1010–680 cm^{-1}): 1002, 983, 900 (s), 870 (s), 745 (sh), 735 (s), 720 (s), 704 cm^{-1} (s); ^{1}H nmr: δ 3.82 (complex d, area 2, J_{PH} = *ca.* 18 Hz), δ 3.4–1.8 (multiplet, area 8); ^{19}F nmr (CH_2Cl_2): δ 23.2 (d, J_{PF} = 1208 Hz); ^{31}P nmr (neat): δ −92.1 (t, J_{FP} = 1211 Hz, of doublets, J_{HP} = 18 Hz).

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A Study of the Relative Reactivity of Phosphines and Amines toward Chloramines and Methyl Iodide

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The relative extent of formation of substituted ammonium and phosphonium salts during the competitive reactions of some *t*-alkylamines and -phosphines with NH_2Cl, CH_3I, and $N(CH_3)_2Cl$ in solution was determined using nuclear magnetic resonance spectroscopy. The relative reactivities of pairs of nucleophiles are explained on the basis of p_π–d_π bonding and steric factors.

Introduction

The syntheses of aminophosphonium chlorides by the chloramination of phosphines,[1,2] (dimethylamino)-phosphonium chlorides by the reaction of phosphines with dimethylchloramine,[3] and 1,1,1-trisubstituted hydrazinium chlorides by the chloramination of trialkylamines[4] are well established. In view of these similar reactions of group V electron-donor compounds with chloramines, it is of interest to find out which of the amines and phosphines react preferentially with chloramines and to try to correlate these reactivities with factors known to affect nucleophilic character[5-7] and bond strength in P–N compounds.[8,9] A comparison of the relative reactivities of amines and phosphines toward the electrophile methyl iodide is also of interest because of differences in electronic structure between methyl iodide and the chloramines.

Experimental Section

Reactants and Their Manipulation.—Trimethylphosphine and triethylphosphine were obtained from K & K Laboratories and checked for purity by nmr spectroscopy.[10] Tributylphosphine was obtained from Carlisle Chemical Works and distilled (bp 125–126° (20 mm); lit.[11] bp 149.5° (50 mm)) prior to use. The infrared spectra of the samples of the above phosphines used showed no P–O stretch[12] in the region 1300–1140 cm^{-1}. Dimethylaminodimethylphosphine was prepared as reported previously.[9] Dibutylaminodibutylphosphine was prepared by the reaction of dibutylchlorophosphine with dibutylamine, bp 114–116° (0.5 mm). *Anal.* Calcd for $(C_4H_9)_2NP(C_4H_9)_2$: C, 70.28; H, 13.27; P, 11.33; N, 5.12. Found: C, 70.16; H, 13.45; P, 11.59; N, 5.32. Chloramine was prepared by the method of Sisler and Mattair,[13] and dimethylchloramine was made by the method of Berg.[14] All solvents were dried over calcium hydride or Linde Molecular Sieve 4A and checked for purity by nmr spectroscopy prior to use.

All transfers and weighing operations involving nonvolatile and air- and moisture-sensitive materials were performed in an inert-atmosphere box (Vacuum Atmospheres Corp. Dri-Train HE-93B) filled with dry nitrogen.

Reaction Procedure and Product Characterization.—Two competing nucleophilic compounds were weighed into a reaction vessel in the drybox. The closed vessel was clamped onto the vacuum line and thoroughly stirred. It was subsequently frozen with liquid nitrogen and degassed. The electrophile (chloramine, dimethylchloramine, or methyl iodide in known amount) for which the nucleophiles were competing was placed in a vessel clamped to the vacuum line and transferred to the reaction vessel by standard vacuum techniques. The mole ratios employed were nucleophile(1):nucleophile(2):electrophile = 1.0:1.0:0.9; typically, 10.0 mmol of each of the two nucleophiles were employed in competition for 9.0 mmol of one of the electrophiles. Ten milliliters of solvent (chloroform, diethyl ether, acetone, or acetonitrile) was used for each 5 ml of nucleophile taken. The reaction flask was allowed to warm to room temperature while stirring was maintained using a stir bar and a magnetic stirrer. The

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